

# Studies on the reaction mechanism of the Fischer–Tropsch synthesis on iron and cobalt

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## Abstract

A new mechanism of the Fischer–Tropsch synthesis is proposed based on the hypothesis that two incompatible mechanisms are involved resting exclusively on methylene and on carbon monoxide insertion, respectively. This hypothesis is reflected by the well known superposition of two Anderson–Schulz–Flory distributions. Experiments with co-feeding of ethene, 1-alkenes and diazomethane as a source of surface methylene and also the carbon number distribution of branched hydrocarbons strongly support the hypothesis of two independent mechanisms and the methylene insertion mechanism of one of them.

Co-feeding of alcohols, the dependence of the ratio of the two mechanisms on the pressure of hydrogen and carbon monoxide and the promoter effect of alkali on iron catalysts also prove the hypothesis of the two mechanisms and point to the carbon monoxide insertion mechanism as the second mechanism that is characterized by the higher growth probability of the resulting Anderson–Schulz–Flory distribution.

Furthermore new interpretations of the crucial steps of C–C linkage and chain termination are given. The insertion of methylene is interpreted by coupling of an alkylidene and a methylene surface species towards a coordinated olefin with the chance of chain growth termination by 1-alkene desorption. For the carbon monoxide insertion mechanism the termination of chain growth is assumed to occur by the formation of 1-alkenes and of alcohols via an alcoholate intermediate.

The new mechanism gives without any exception a sound interpretation of a great variety of experiments and contributes also to the interpretation of the promoter effect of alkali and of the different performance of cobalt and iron catalysts.

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**Keywords:** Fischer–Tropsch synthesis; Reaction mechanism; Iron catalyst; Cobalt catalysts

## 1. Introduction

Although numerous studies over 70 years concern the mechanism of the Fischer–Tropsch synthesis this subject still remains controversial. At present many authors favour the CH<sub>2</sub> insertion mechanism as dominant for the F–T synthesis. However, the formation of oxygenates is hardly feasible via the CH<sub>2</sub> insertion mechanism. Therefore, oxygenates are assumed to be formed via the CO insertion mechanism. In order to explain both the formation of hydrocarbons and oxygenates Dry [1] proposed a

mechanism that involves both CH<sub>2</sub> and CO as active surface intermediates.

For all Fischer–Tropsch catalysts deviations from the ideal Anderson–Schulz–Flory (ASF) distribution are observed. For both iron and cobalt catalysts product distributions can be represented by superposition of two ASF distributions characterized by the growth probabilities  $\alpha_1$ ,  $\alpha_2$ , and  $f_2$  the mass fraction of distribution 2 characterized by  $\alpha_2$  [2–4]. The hypothesis that these deviations can be exclusively traced back to readsorption of 1-alkenes and secondary chain propagation and that the CH<sub>2</sub> insertion mechanism is the exclusive one that could be definitely excluded by means of stoichiometric calculations on the basis of 1-alkene and ethene co-feeding experiments [5,6]. These experiments using a cobalt catalyst have shown

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that readsorbed 1-alkenes and ethene grow with the probability  $\alpha_1$  [4,6,7].

Based on these 1-alkene and ethene co-feeding experiments with cobalt catalysts and on the promoter effect of alkali on iron catalysts we have drawn the conclusion that the two superimposed ASF distributions with different chain growth probabilities are the result of different chain growth mechanisms that are not compatible [6].

The aim of the present study is to develop a consistent hypothesis of the mechanism of the F–T synthesis on the basis of co-feeding experiments with 1-alkenes, ethene, alcohols and  $\text{CH}_2\text{N}_2$ , as a source of  $\text{CH}_2$ , and on the formation of branched hydrocarbons, alcohols and aldehydes. Also the promoter effect of alkali ( $\text{K}_2\text{O}/\text{K}_2\text{CO}_3$ ) on iron catalysts is taken into consideration.

The formulation of the novel mechanism follows the knowledge of analogous reactions in homogeneous catalysis and should give a detailed insight in the crucial step of C–C linkage.

## 2. Results

The development of the novel mechanism is based on experimental studies of many authors who employed different types of iron and cobalt catalysts. However, this variety of catalysts causes no problem for discussions about the mechanism since with the exception of the promoter effect of alkali additives have only a moderate influence on the selectivity of the synthesis on iron and cobalt catalysts. Many experiments show that the metal (Co or Fe) dominates the properties of the catalyst. For example a Co-catalyst without any additives and Co supported on  $\text{SiO}_2/\text{ZrO}_2$  show the same dependencies of the carbon number distribution on the partial pressures of hydrogen and carbon monoxide [8].

The superposition of two ASF distributions is regarded as the result of different chain growth mechanisms that are not compatible. In preceding studies it has been proposed that the distribution characterized by the lower growth probability  $\alpha_1$  is related to the  $\text{CH}_2$ -insertion mechanism [4]. This hypothesis is strongly supported by experimental data of Maitlis and co-workers [9] who studied the Fischer–Tropsch synthesis on a Co/ $\text{SiO}_2$  catalyst. As a refinement of the studies of Brady and Pettit [10] they could definitely show by co-feeding of  $^{13}\text{CH}_2\text{N}_2$  to syngas  $^{12}\text{CO}/\text{H}_2$  that the  $^{13}\text{CH}_2$  intermediates react in the same way as surface  $^{12}\text{CH}_2$  groups formed from  $^{12}\text{CO}/\text{H}_2$  leading to random incorporation into the formed hydrocarbons. If hydrocarbons were formed exclusively via  $\text{CH}_2$  insertion a constant fraction of incorporated  $^{13}\text{C}$  would be expected over all hydrocarbons. However, the experiments revealed a strong decrease of  $^{13}\text{C}$  incorporation with increasing carbon number, an observation which was not commented on by the authors. The growth probability due to the hydrocarbons with incorporated  $^{13}\text{CH}_2$  as we have calculated from the data of Maitlis and co-workers comes out at  $\alpha \approx 0.5$  in accordance with the value of  $\alpha_1 \approx 0.47$  evaluated for the synthesis on cobalt at 513 K [8].

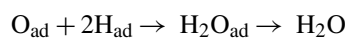
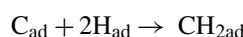
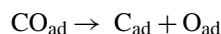
However, the nature of the synthesis related to the distribution characterized by the higher growth probability  $\alpha_2$  has remained in question. In the present study we have related this distribution

to the CO insertion mechanism, initially proposed by Pichler and Schulz [11], for both the synthesis of hydrocarbons and oxygenates. This hypothesis is suggested by the finding that mechanism 1,  $\text{CH}_2$  insertion, is favoured with increasing  $p_{\text{H}_2}$  and mechanism 2, CO insertion, is favoured with increasing  $p_{\text{CO}}$  [12].

First of all the proposed mechanism is explained in detail. In Section 3 the reasons for these formulations are thoroughly discussed.

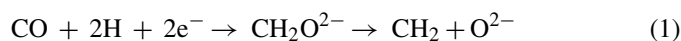
### 2.1. Formation of the monomer $\text{CH}_2$

The proposal of the early carbide mechanism involves C–O bond dissociation prior to reaction with hydrogen to form  $\text{CH}_2$ :



Later direct proof for this dissociation and the existence of  $\text{CH}_2$  on the surface could be obtained by spectroscopic studies as reported in the review article of Hindermann et al. [13]. This route is assumed as dominant until today [14]. But also a successive hydrogenation of adsorbed CO has been proposed [11].

In this case ensembles of surface metal atoms (Fe or Co) in a low formal oxidation state  $x$  ( $0 < x < 1$ ) are envisaged to act as reservoir of hydride equivalents for the formal reduction of CO to afford a “formyl” species. Subsequent C–O bond cleavage gives coordinated methylene and oxide ion which is transformed to  $\text{OH}^-$  and  $\text{H}_2\text{O}$  [15]:

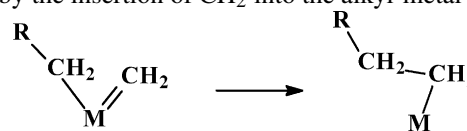


The sequence of steps requires at least two metal atoms: one of them accepts the oxide ion and the other one carries the carbon chain.

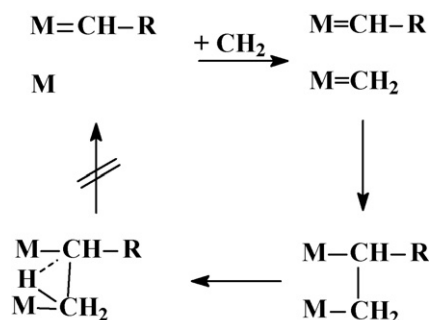
We assume that both routes are likely. Since it is impossible to separate dissociation and hydrogenation under real reaction conditions of F–T synthesis there is hardly a chance to find out which is the dominant route towards  $\text{CH}_2$ .

### 2.2. Mechanism 1: monomer $\text{CH}_2$ (Schemes 2 and 3)

Biloen and Sachtler [16] described the formation of hydrocarbons by the insertion of  $\text{CH}_2$  into the alkyl-metal bond.



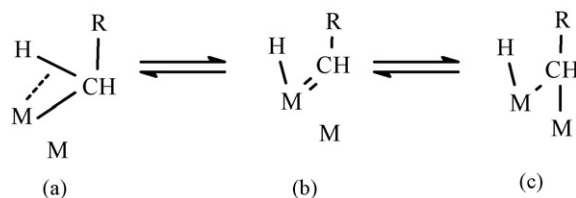
The formation of 1-alkenes is assumed to occur via  $\beta$ -H-elimination. However, some authors prefer coupling of alkylidene with  $\text{CH}_2$ . Joyner [17] has proposed a complete cycle of chain prolongation by  $\text{CH}_2$ , Scheme 1.



Scheme 1. Alkylidene–methylene coupling proposed by Joyner [17].

However, this mechanism ignores the presence of surface M–H functions and is ruled out by the experiments of Brady and Pettit [10] who showed that only in the presence of hydrogen 1-alkenes are formed. Obviously in the mechanism proposed by Joyner the internal isomerisation involving an 1,2-hydrogen shift is unlikely. The other authors who assumed coupling of alkylidene and methylene did not present a complete cycle of chain prolongation.

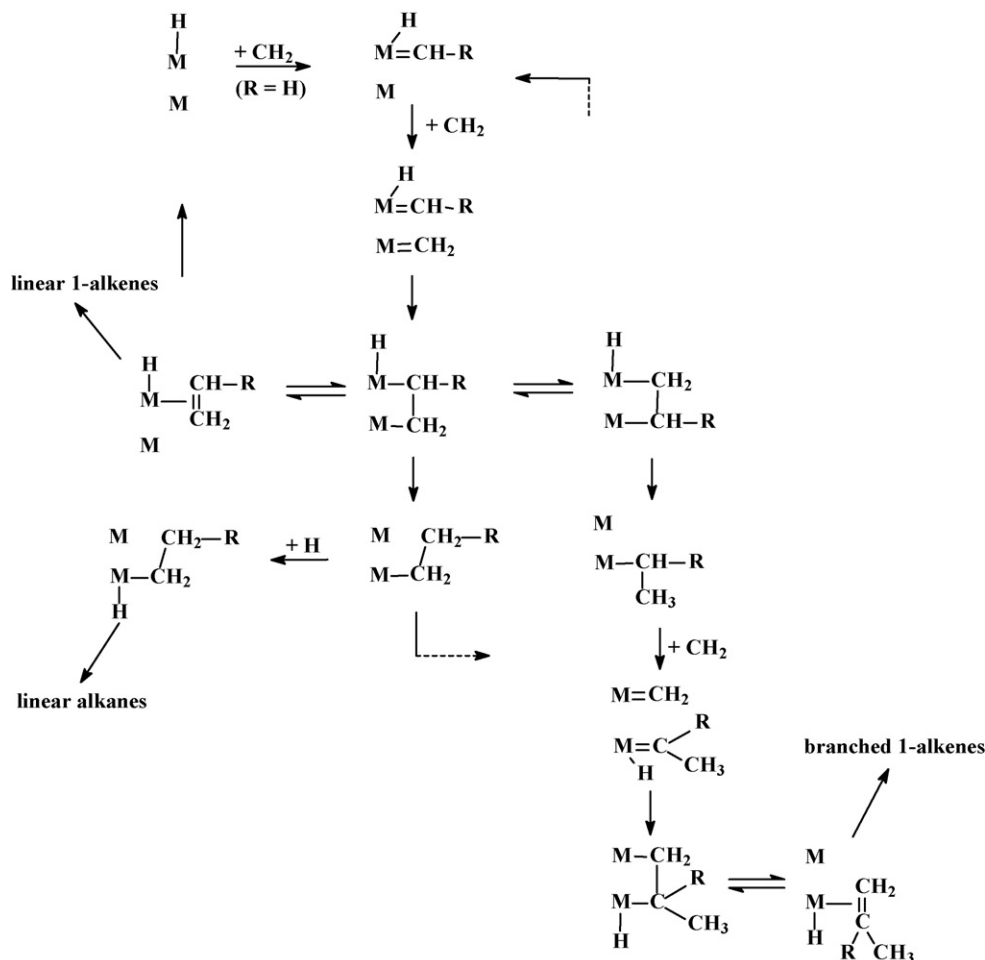
We have modified the alkylidene–methylene coupling and present here a complete cycle of chain prolongation by CH<sub>2</sub> that is in accordance with the experiments of Brady and Pet-



Scheme 2. Valence-bond representations of the (C, H)-chelating ("agostic") bonding mode in a two-metal-atom site.

tit. In order to formally insert CH<sub>2</sub> the growing alkyl chain must attain a situation of metal-to-carbon bonding that favours CH<sub>2</sub> insertion over coupling of two CHR groups (R = H, alkyl) [18]. A (C, H)-chelating coordination mode characterized by agostic M–H–C interaction [19] (Scheme 2) would meet this requirement. When compared with  $\sigma$ -alkylmetal bonding the (C, H)-chelating bonding mode is characterized by a longer C–H bond and a smaller HCM angle and requires higher activation energies for reductive elimination of alkane,  $\beta$ -H elimination, insertion of CO or olefin; but lower activation energies for alkylidene–methylene coupling.

Valence bond representation b (Scheme 2) is chosen to demonstrate the particular reactivity. For the sake of clarity M–M bonding does not appear in the valence bond representa-



Scheme 3. Mechanism 1 (M = Fe, Co).

tion of the dimetal site because of its metallic nature. This novel mechanism substantially differs from the formal  $\text{CH}_2$  insertion mechanism assumed in most preceding studies.

In Scheme 3 a simplified representation has been chosen for an instructive interpretation of chain growth, incorporation of ethene or 1-alkene, and for chain branching.

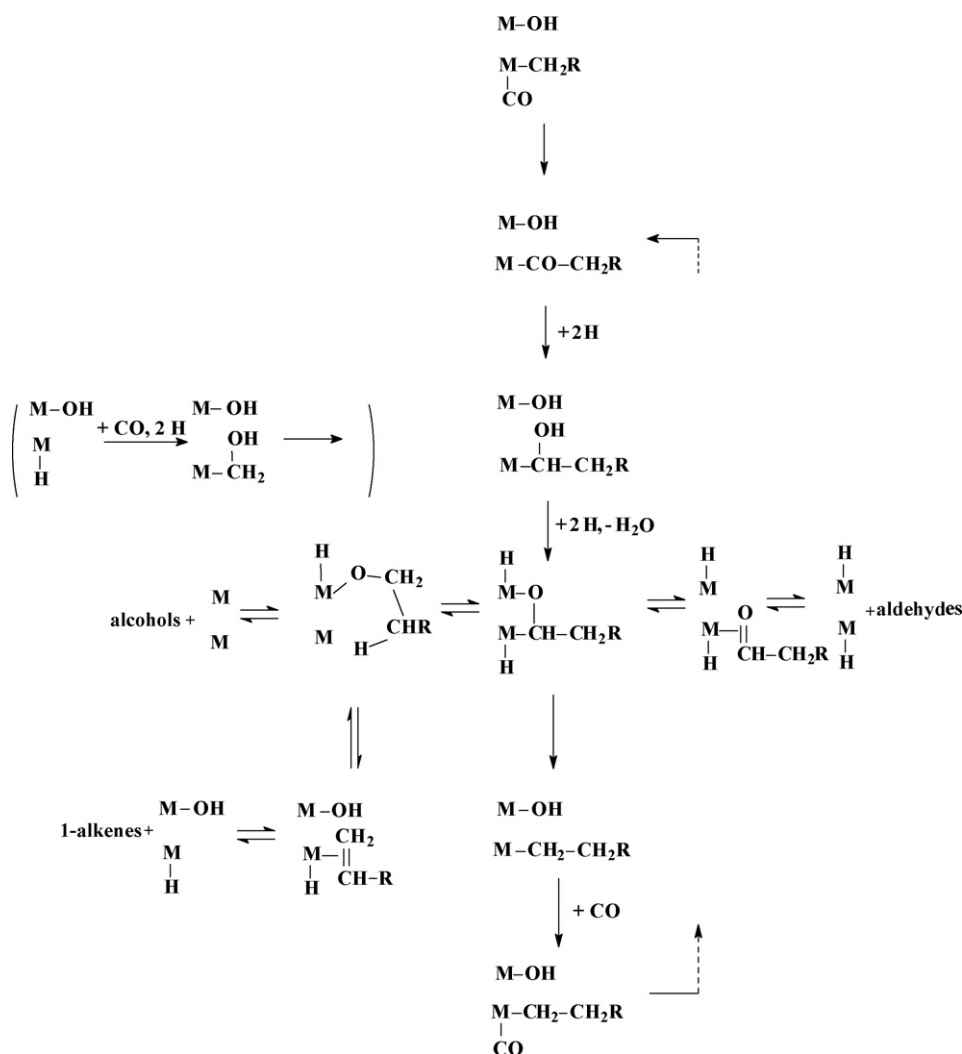
As an arbitrary start, an alkyl metal species is transformed via  $\alpha$ -H-elimination to the (C, H)-chelating ground state (written as (b) of Scheme 2) where an adjacent metal centre accommodates a migrating  $\text{CH}_2$  unit. Alkylidene–methylene coupling affords a coordinated olefin. Propeller-type mobility of the olefin ligand renders possible  $\text{CH}_3$  branching of the growing chain as demonstrated by the scheme. Each growth cycle consists of  $\alpha$ -H-elimination,  $\text{CH}_2$ -coordination to the adjacent metal centre, alkylidene–methylene coupling, and reductive coupling leading back to the alkyl metal state. Chain propagation is started from a methylene group and terminated by desorption of 1-alkenes or alkanes.

The growth probability that is determined by the ratio of rates of the formation of the alkyl intermediate and of the desorption of 1-alkenes and to a minor extent of alkanes can be

regarded as independent of the concentration of hydrogen in accordance with experimental results [12]. This independence of the hydrogen concentration cannot be explained by the usual assumption of  $\beta$ -H-elimination from alkyl metal followed by 1-alkene desorption. With increasing hydrogen concentration a reduced  $\beta$ -H-elimination and correspondingly increased growth probability would be expected in contradiction to the experimental results.

### 2.3. Mechanism 2: monomer CO (Scheme 4)

Insertion of CO proceeds as in alkyl(carbonyl)metal complexes by alkyl migration. Reductive elimination of water and, finally, C–O cleavage by altogether four H-equivalents will lead back to the starting situation. The chain growth is started with a methylene group formed by hydrogenation of adsorbed CO, see Section 2.1. It is assumed that termination occurs by conversion of the C,O-bridging aldehyde intermediate to alcoholate which is either dehydrated via  $\beta$ -CH-activation to afford a M–OH function and a hydrido (olefin) metal species or to a minor extent is converted to alcohol.



This route of termination is regarded as reversible and thus allows the incorporation of co-fed alcohol causing initiation of the F–T synthesis via the C,O-bridging aldehyde intermediate. But co-fed alcohol can also be dehydrated to olefin as expressed by the novel mechanism and in line with experiments of Emmett and co-workers [20–23].

Tau et al. [24] have shown that alcohol and aldehyde are reversibly converted on iron. Hutchings et al. [25] interpreted this redox process by the adsorption of alcohol via oxygen. This reversibility via the alcoholate and the C,O-bridging aldehyde intermediate is also expressed in the novel mechanism.

The growth probability is determined by the ratio of rates of the conversion of the C,O-bridging aldehyde intermediate towards the alkyl metal species and towards liberation of 1-alkene and alcohol. Both reactions can be regarded as independent of the concentration of hydrogen in accordance with experimental results [8,12].

The hydrido (olefin) metal intermediate is unlikely to arise from  $\beta$ -H-elimination in the growing chain because that would lead to a  $p_{H_2}$  dependent growth probability  $\alpha_2$  in contradiction to the experimental results.

### 3. Discussion

The incompatibility of both mechanisms is indicated by the strict superposition of both ASF distributions that is demonstrated in Fig. 1 for a cobalt catalyst and in Fig. 2 for iron catalysts, unpromoted and promoted with alkali ( $K_2O/K_2CO_3$ ). This incompatibility may find an explanation in the fact that in mechanism 1 the formation of the monomer  $CH_2$  and consequently the removal of  $H_2O$  occur apart from the growing chain while in mechanism 2 the removal of  $H_2O$  occurs in the course of chain growth. We assume that in mechanism 1 a coordination

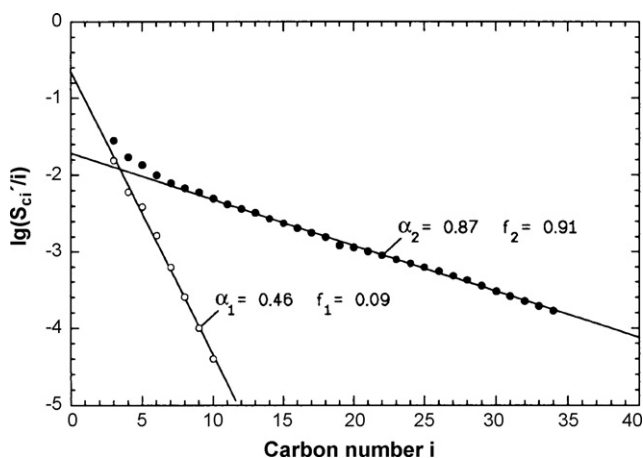


Fig. 1. Bimodal ASF distribution obtained on Co catalyst.  $T=493$  K,  $p_{H_2}=3$  bar,  $p_{CO}=1.5$  bar, pure precipitated and reduced cobalt.  $S_{C_i}$  the carbon selectivity of hydrocarbons of carbon number  $i$  is defined by the mass of carbon in the components related to the mass of carbon of all hydrocarbons in the reaction product. Corresponding to the Anderson–Schulz–Flory equation  $\log(S_{C_i}/i) = (1 - \alpha)^2 \alpha^{i-1}$  the slopes of the straight lines in the diagram  $\log(S_{C_i}/i)$  vs.  $i$  give  $\alpha_1$  and  $\alpha_2$ . The open symbols represent  $S_{C_{i,exp.}}/i$  of distribution 1, that is the difference of the experimentally obtained value  $S_{C_{i,exp.}}/i$  and the estimated value for distribution 2  $S_{C_{i,2}}/i$ . For a detailed description see Ref. [8].

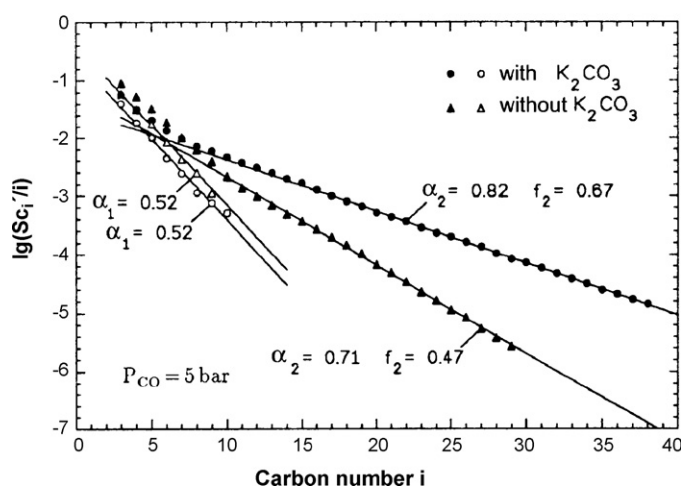
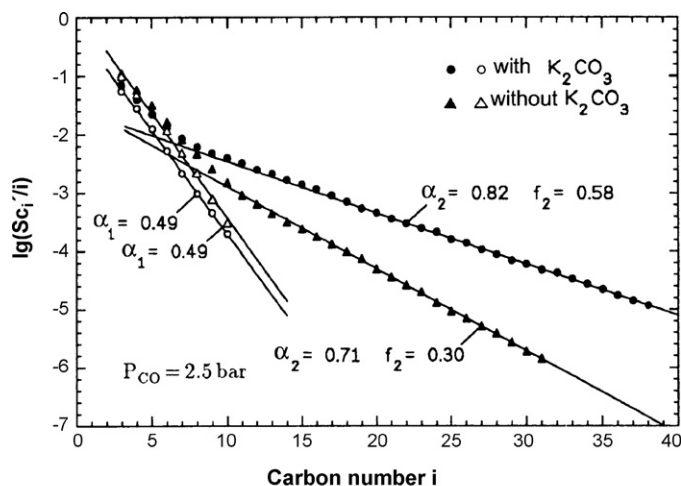


Fig. 2. Promoter effect of  $K_2O/K_2CO_3$  on ASF distribution, iron catalysts. Fe(0) and Fe(2 wt%  $K_2CO_3$ ),  $T=493$  K,  $p_{H_2}=5$  bar,  $p_{CO}=2.5$  and 5 bar. The open symbols represent  $S_{C_{i,1}}/i$  of distribution 1, that is the difference of the experimentally obtained value  $S_{C_{i,exp.}}/i$  and the estimated value for distribution 2,  $S_{C_{i,2}}/i$ . For the definition of  $S_{C_i}$  see Fig. 1.

site for an arriving  $CH_2$  is always available. In mechanism 2, however, the adjacent site is assumed to be permanently occupied by OH so that there is no chance for  $\alpha$ -H-elimination and the formation of the alkylidene species. As a precondition chain growth must be faster than hydrogenation of coordinated OH.

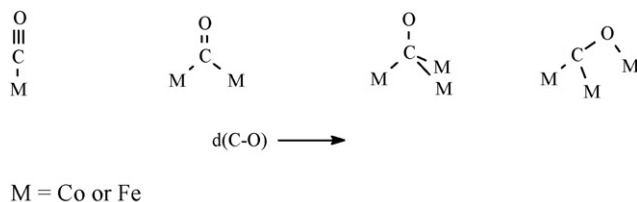
In addition we assume that different active sites of specific preference with respect to these mechanisms play a marked role. The ratio of such sites may depend on the composition of the adsorption layer.

#### 3.1. Comparison of iron and cobalt catalysts

The fraction of hydrocarbons associated with mechanism 1 is for iron considerably higher than for cobalt,  $f_1 \approx 0.4$  and  $f_1 \approx 0.1$ , respectively, see Figs. 1 and 2.

When compared with cobalt the higher oxophilicity of iron favours coordination of oxygen atoms as demonstrated on the right-hand side of Scheme 5. The resulting polarisation corresponds with oxidation of iron and a lower affinity for CO. The cleavage of a C–O bond and the removal of oxygen from the





Scheme 5. Species of chemisorbed carbon monoxide.

catalyst surface strongly depend on  $p_{\text{H}_2}$  so that the tendency of  $\text{CH}_2$  formation and finally the share of mechanism 1 increases with increasing  $p_{\text{H}_2}$  while elevated  $p_{\text{CO}}$  favour site-poisoning and mechanism 2.

When compared with iron cobalt shows a higher affinity for CO ligands as demonstrated on the left-hand side of Scheme 5. Mechanism 2 dominates and increases with  $p_{\text{CO}}$ .

### 3.2. The promoter effect of alkali ( $\text{K}_2\text{O}/\text{K}_2\text{CO}_3$ )

The comparison of product distributions obtained on alkali promoted and unpromoted iron catalysts has shown that the distribution characterized by the lower growth probability  $\alpha_1$  is not affected by the promoter while the growth probability  $\alpha_2$  and the fraction  $f_2$  are considerably increased by addition of alkali, Fig. 2.

Studies on the adsorption of CO and  $\text{H}_2$  on promoted and unpromoted iron catalysts have revealed that addition of alkali causes a considerably increased strength of CO adsorption but only a slightly decreased one of hydrogen [26–29].

The electronic promoter effect arises from potassium which, as a strongly electropositive element donates electronic charge in the 3d orbitals via the oxygen bridge [30]. Formally one has to deal with a species of the type  $\text{Fe}^{\delta-}-\text{O}-\text{K}^{\delta+}$  where  $\delta$  stands for the fractional charge donated by the K atom. This additional charge in the 3d shell of iron enhances the “ $d_{\pi}-p_{\pi}$  back donation” from the  $t_{2g}$  subshell of an iron cluster into the antibonding  $2\pi^*$  orbital of CO resulting in an increased CO adsorption energy. Furthermore it is well known from coordination chemistry that hydroxyl groups are extremely poor  $\pi$ -acceptor ligands thus “ $d_{\pi}-p_{\pi}$  back binding” as additional bond strengthening effect does not occur. Bonding between the metal and these ligands is mainly effected by  $\sigma$ -donation of ligand lone pairs. As the additional charge at the iron centre is taken up as in the species  $\text{Fe}^{\delta-}-\text{O}-\text{K}^{\delta+}$   $\sigma$ -donation from OH and  $\text{H}_2\text{O}$  molecules will be reduced with the consequence that the tendency for binding OH and  $\text{H}_2\text{O}$  ligands to form the precursor product of iron oxide decreases and the reducibility of iron oxides is increased. This effect could be clearly demonstrated by Guglielminotti et al. [31] and by König et al. [30].

On the whole the promoter effect of alkali on iron causes a shift of the metallic properties towards cobalt and thus with respect to the chemisorption of CO to the left-hand side of Scheme 5.

Since the oxophilicity of Fe is reduced by addition of alkali the tendency towards terminal CO ligands is increased. Furthermore an enhanced negative charge of the alkyl group is expected

as the consequence of the increased negative charge of iron. Both effects favour the alkyl migration leading to CO insertion. By this way the increased fraction of mechanism 2 and the increased growth probability  $\alpha_2$  find a sound interpretation. Furthermore the fraction  $f_2$  is increased with increasing  $p_{\text{CO}}$  as demonstrated in Fig. 2. These effects strongly support the hypothesis of superimposed mechanisms and the CO insertion as responsible for mechanism 2.

### 3.3. Incorporation of ethene and 1-alkenes

The novel mechanism, as given in Schemes 3 and 4 demonstrates that incorporation of ethene and 1-alkenes and subsequent chain growth are feasible only via mechanism 1 ( $\text{CH}_2$  insertion) as the reverse of the formation of 1-alkenes so that the growth probability of incorporated 1-alkenes or ethene is expected as  $\alpha_1$  in accordance with the experimental results of several authors [4,5,7]. Mechanism 2 (CO insertion) offers no chance for the incorporation of ethene and 1-alkenes.

### 3.4. Synthesis of branched hydrocarbons

A detailed analysis of F–T products obtained on iron and cobalt catalysts by van Steen [32] and Schulz et al. [14,33] revealed an exponential decrease of the probability of branching with increasing carbon number as demonstrated in Fig. 3. The probability of branching were calculated on the basis of the model of nontrivial surface polymerisation proposed by Schulz et al. [34]. Up to now a sound interpretation of these results is lacking. The novel model, however, gives a simple and sound interpretation with the assumption that branching occurs only via mechanism 1 ( $\text{CH}_2$  insertion) characterized by the growth probability  $\alpha_1$  of about 0.5. The formal growth probability of

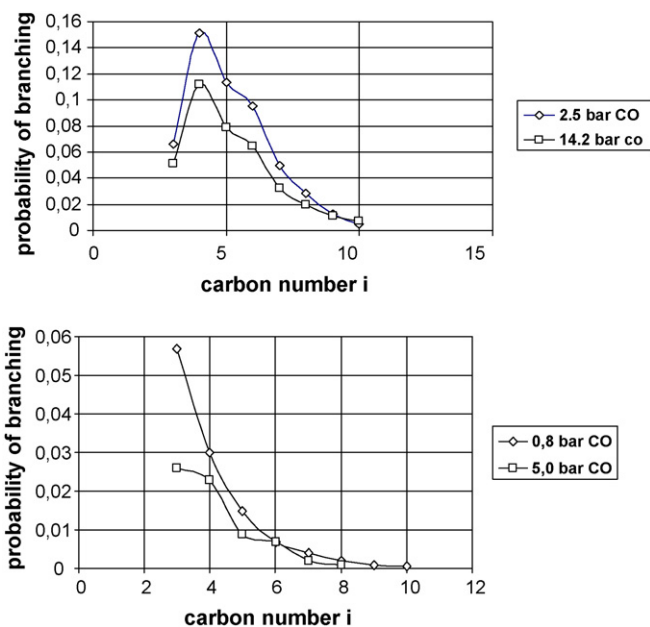


Fig. 3. Probability of branching vs. carbon number for—iron catalyst Fe–Cu–Al–K:  $p_{\text{H}_2} = 9.9$  bar,  $T = 523$  K [32]; cobalt catalyst Co–Mg:  $p_{\text{H}_2} = 2.7$  bar,  $T = 483$  K [32].

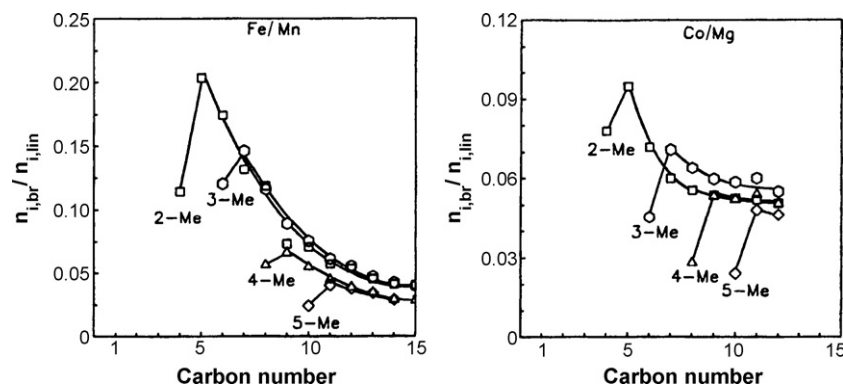


Fig. 4. Ratio of branched and linear hydrocarbons vs. carbon number—iron catalyst Fe–Cu–Al–K:  $p_{H_2} = 9.9$  bar,  $T = 523$  K [32]; cobalt catalyst Co–Mg:  $p_{H_2} = 2.7$  bar,  $T = 483$  K [32].

branching evaluated from the data of van Steen approximately resulted at 0.4–0.6. This hypothesis gives also an explanation for the higher fraction of branched hydrocarbons in products obtained over iron catalysts as the fraction of products formed via mechanism 1 is higher for iron than for cobalt catalysts. The branching probability of the step  $C_3 \rightarrow C_4$  is lower than the following one obviously due to steric reasons.

The direct plot of experimental data shows that the fraction of monomethyl branched hydrocarbons decreases with increasing carbon number and changes into a constant level, Fig. 4.

This level is for cobalt higher than for iron. Since mechanism 2 dominates the carbon number distribution in the range of elevated carbon numbers the constant molar fraction of branched hydrocarbons must be assigned to mechanism 2. If branching could occur at every cycle of chain prolongation, for example by transfer of  $CH_3$  groups as proposed for the original version of the CO insertion mechanism [11], we would expect an increasing fraction of branched hydrocarbons with increasing carbon number and not a constant one. Therefore, it is concluded that on the course of chain prolongation by CO insertion no branching occurs. However, branching can occur on the course of incorporation of alcohols as shown by the experiments of Kummer and Emmett [22] with co-feeding of  $^{14}C$ -labelled propanol. They observed a marked formation of  $^{14}C$ -labelled isobutene.

For the synthesis on cobalt Schulz [14] observed a markedly increased formation of  $C_4$  alcohols by co-feeding of propene and interpreted this result with the parallel hydroformylation of propene. Since via this reaction also isobutanol is formed another way for the formation of branched hydrocarbons would be opened within mechanism 2.

### 3.5. Incorporation of alcohols and the formation of oxygenates in F–T synthesis

Co-feeding of alcohols leads to an increased rate of hydrocarbon formation as shown in early experiments of Emmett and co-workers [20–23] using  $^{14}C$ -labelled alcohols. These experiments were carried out in order to support the formerly favoured hydroxy-carbene mechanism. However, these results can also be regarded for the discussion of the CO insertion mechanism as alcohol can be incorporated via the reverse of the formation of

alcohol as demonstrated in Scheme 4. These co-feeding experiments were confirmed by Shi and Davis [35] for Co catalysts and the incorporation of ethanol. Furthermore in their study the argument that ethanol may be dehydrated to ethene, readsorbed, incorporated and followed by subsequent chain growth via  $CH_2$  insertion could be excluded as co-fed ethanol is much faster incorporated than ethene.

For both ethanol and propanol co-feeding of methylene- and methyl labelled alcohols show nearly the same activity distribution of formed hydrocarbons indicating that C–C bonds of incorporated alcohols are not cleaved. Accordingly, the formation of methane is very small [20,22]. For co-feeding of  $^{14}C$ -labelled ethanol and 1-propanol the molar  $^{14}C$ -activity of hydrocarbons formed on iron catalysts (unpromoted and promoted with alkali) show in the range up to  $C_6$  a decelerating increase and then a constant value up to the wax fraction as shown for ethanol in Fig. 5. For cobalt catalysts a nearly constant  $^{14}C$ -activity was found for the entire range of carbon numbers up to the wax fraction. Propionaldehyde is incorporated to a similar extent as 1-propanol [23].

All these experiments clearly show that incorporation of alcohols and subsequent chain growth can only occur in the course of mechanism 2 (CO insertion) with the high growth probability  $\alpha_2$  dominating the range of elevated carbon numbers and

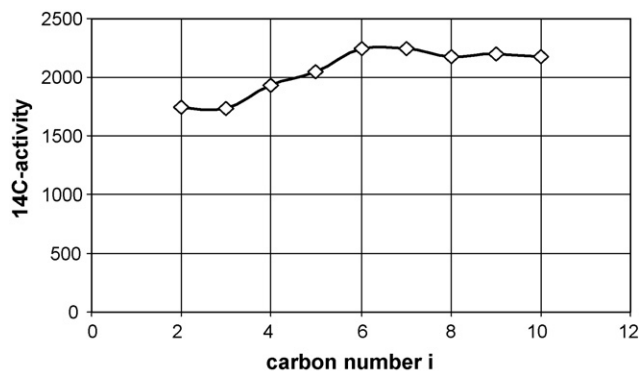


Fig. 5. Molar  $^{14}C$ -activity of hydrocarbons vs. carbon number of co-feeding experiments with ethanol, labelled in 1-position.  $^{14}C$ -activity of wax (averaged carbon number 26) = 2200. Fe– $Al_2O_3$  2.8%– $ThO_2$  1.4%,  $T = 493$  K,  $H_2/CO = 1$  [20].

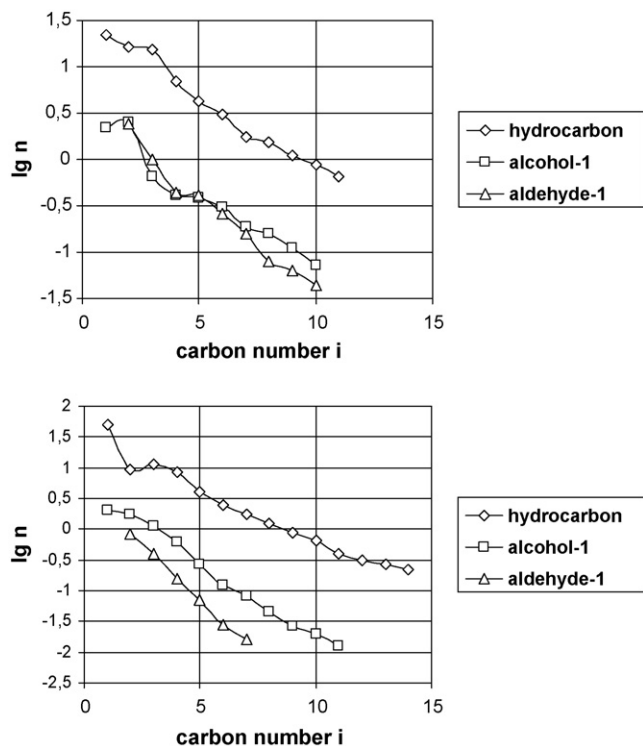


Fig. 6. Carbon number distribution of linear hydrocarbons, linear alcohols (1) and linear aldehydes [32]. Catalyst Fe(100)–Al<sub>2</sub>O<sub>3</sub>(37)–Cu<sub>3</sub>–K<sub>2</sub>O(2);  $T=523$  K,  $p_{\text{H}_2}=10.1$  bar,  $p_{\text{CO}}=19.4$  bar. Catalyst Co(100)–SiO<sub>2</sub>(465);  $T=483$  K,  $p_{\text{H}_2}=9.6$  bar,  $p_{\text{CO}}=19.7$  bar.

that the hydroxyalkyl group of incorporated alcohol is inevitably hydrogenated to a CH<sub>2</sub>-group.

Furthermore the co-feeding experiments [20–23] have revealed that ethanol and propanol are to a considerable extent converted to ethene and ethane or to propene and propane, respectively. As shown in Scheme 4 the hydrogenation of the [C,O]-coordinated aldehyde leads either to the formation of a CH<sub>2</sub> group or by hydrogenolysis of the M–C bond to an alcoholate surface species. This intermediate is either converted to alcohol or hydrocarbon as chain termination. Alcohols may be converted in a reverse reaction to hydrocarbons via this alcoholate intermediate. Therefore the assumption is justified that hydrocarbons are exclusively formed by dehydration of the alcoholate intermediate.

Alcohols and aldehydes are minor products of the F–T synthesis on iron and on cobalt. Because of the consecutive hydrogenation of alcohol via the alcoholate towards hydrocarbons the yield of alcohols depends strongly on reaction conditions. For example studies by Claeys and Schulz [36] have shown that the yield of alcohols strongly decreases with increasing particle size of the catalyst due to the increased resident time of products favouring the consecutive hydrogenation. We must further assume that the degree of hydrogenation and readsorption increases with increasing carbon number due to the decreasing volatility of alcohols. Therefore, for both iron and cobalt catalysts the fraction of alcohol decreases with increasing carbon number as shown in Fig. 6. Alcohols and aldehydes form the major fraction of oxygenates but various

routes lead to a variety of compounds such as ketones, esters and acids.

### 3.6. Interdependence of F–T synthesis and water gas shift reaction for iron catalysts

When iron catalysts are employed the reaction product water formed in the F–T synthesis subsequently reacts with CO forming H<sub>2</sub> and CO<sub>2</sub>. Kinetic studies have shown that water is mainly desorbed and then again adsorbed to react with CO [37,38]. The water gas shift reaction may be written by the formal equations:



An interdependence between the F–T synthesis and the water gas shift reaction may occur via Eq. (3) causing deactivation of F–T active centres operating mechanism 1. In this interaction alkali as a promoter plays a crucial role as already mentioned in Section 3.2.

Studies of König et al. [30] have shown that the growth probability  $\alpha_2$  and thus the cycle of hydrocarbon formation following mechanism 2 is not affected by an increase of  $p_{\text{H}_2\text{O}}$ . However, with increasing  $p_{\text{H}_2\text{O}}$  the reaction rate with respect to mechanism 1 decreases. This result corresponds to the rate equation for the F–T synthesis on iron given by Arakawa and Bell [26] showing a decreasing rate with increasing  $p_{\text{H}_2\text{O}}$ .

$$-r_{\text{CO}+\text{H}_2} = \frac{k p_{\text{CO}} p_{\text{H}_2}^2}{p_{\text{CO}} p_{\text{H}_2} + b p_{\text{H}_2\text{O}}}$$

With increasing  $p_{\text{H}_2\text{O}}$  the growth probability  $\alpha_1$  slightly decreases indicating an interruption of the growth cycle of mechanism 1.

## 4. Conclusion

The co-feeding experiments with ethene and 1-alkenes, the dependence of the fraction of branched hydrocarbons on the carbon number, the growth probability of hydrocarbons obtained by decomposition of CH<sub>2</sub>N<sub>2</sub> in the presence of hydrogen and in particular the CH<sub>2</sub>N<sub>2</sub> co-feeding experiments of Maitlis and co-worker suggest that products attributed to distribution 1 are formed via the CH<sub>2</sub> insertion mechanism.

The co-feeding experiments with alcohol, the formation of alcohols and aldehydes, the increase of fraction  $f_2$  with increasing  $p_{\text{CO}}$ , and its decrease with increasing  $p_{\text{H}_2}$  are strong arguments for the assumption that the products assigned to distribution 2 characterized by  $\alpha_2$  are formed via the CO insertion mechanism. The initiation of chain growth by incorporated alcohol to form hydrocarbons gives evidence that intermediate aldehyde and H–C–OH groups are hydrogenated to CH<sub>2</sub> groups.

This great variety of experiments presented by many authors supports without exception the hypothesis that two incompatible mechanisms are involved resting exclusively on –CH<sub>2</sub> and on CO insertion, respectively.



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