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Construction of the Fischer–Tropsch regime with cobalt catalysts[☆]

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Abstract

Changes of activity and selectivity during the initial phases of Fischer–Tropsch (FT) synthesis have been measured with three promoted cobalt catalysts. It is shown that the FT regime is formed in situ in a slow process lasting several days. A "construction" of the "true FT catalyst" is therefore assumed. Taking into account complementary investigations, this construction is assigned to the segregation of the catalyst surface caused by strong CO chemisorption. This process would be accompanied by an increase of the number of active sites and their disproportionation into sites of higher and lower coordinations, which would exhibit different catalytic properties. The observed initial activity and selectivity changes are well to be explained with this concept. © 2002 Published by Elsevier Science B.V.

Keywords: Cobalt catalyst; Fischer–Tropsch regime; CO

1. Introduction

Changes of product composition in the initial stages of conversion on the surface of a solid catalyst may have several causes. In a fixed bed reactor when the flow of reactants is established, the partial pressures will shift and the reactor temperature will be affected by the reaction enthalpies. Adsorption of educts, products and intermediates will provide a dynamic coverage of the surface. Additionally, the catalyst itself can undergo structural and compositional changes. Thus, it can be that the "true catalyst" is formed and stable only in situ.

The multicompound composition of Fischer–Tropsch (FT) products reflects a complex set of surface reactions. It can be regarded as a source of information about the involved active sites. As the product composition changes with time, it mirrors changes of the catalytic system. With this concept in mind, initial changes of reaction rate and product composition during FT synthesis with three promoted cobalt catalysts are presented and discussed in this paper.

2. Experimental

The cobalt catalysts have been prepared by quick precipitation with an ammonia solution being added to the nitrates solution in which small SiO_2 particles (aerosil, $d_p \sim 200$ Å) had been suspended [1] to obtain the compositions (weight ratios): 100 Co:100 SiO_2 (aerosil):11 Zr:0.45 Pt; 104 Co:100 SiO_2 (aerosil):9 Re; 100 Co:100 SiO_2 (aerosil):14 Ir.

Platinum was added to the zirkonia promoted catalyst by impregnation of the dried precipitate with a H_2PtCl_6 solution. The precipitates were dried at 393 K, ground and sieved ($d_p \ll 0.1$ mm), diluted (weight ratio, 1:10) with fused silica spheres ($d_p =$ 0.25–0.4 mm) and 6 ml of this mixture, corresponding to 0.68 g of cobalt, filled into the fused silica

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reactor tube of 9 mm inner diameter. The catalysts were calcined and reduced in situ (calcination: argon flow of 40 ml(NTP)/min, 1 bar, heating 2 K/min up to 973 K, 2 h at this temperature; reduction: gas flow 40 ml(NTP, H_2:Ar = 1:3)/min, heating 2 K/min up to 973 K isothermal at this temperature until H_2O from reduction was no longer to be detected). The conditions of synthesis were 463 K, 5 bar, $H_2/CO = 1.9$, GHSV $= 300\,h^{-1}$ (GHSV referred to the catalyst bed volume of 6 ml).

Apparatus and procedure for FT synthesis had specifically been developed: small catalyst particles for only negligible mass transfer influences, isothermal operation through high catalyst dilution, homogeneous gas flow and low pressure drop by application of relatively big fused silica dilution particles, precise measurement and control of flow and composition of in- and out-going streams for accurate mass balances (also with the help of the internal standards) and time resolution of reaction rate and selectivity by means of quick ampoule sampling ($\leq$0.1 s) from the hot (473 K) gaseous product stream [2–4] after passing a hot trap. GC analysis, developed for the ampoule samples, covered the range C_1 to ca. C_{16} with high precision, high resolution and no discernible discrimination applying a temperature programme from 353 to 493 K and that also in a version with olefin precolumn hydrogenation as used for the investigation of chain branching [2]. Importance for this work has also been the earlier development of a kinetic model [5–7]. This model allows to transform the observed multicompound product composition data into a set of kinetic coefficients of the reactions of chain prolongation, termination and branching, each as a function of carbon number. Additionally, the olefin reactions readsorption for growth, hydrogenation and double bond shift are quantified with dependence on carbon number.

3. Results and discussion

3.1. Development of activity with time

The activity of the three cobalt catalysts has been determined as CO conversion with dependence on time. CO_2 was not present in the product stream. Thus, CO conversion equalled the yield of organic compounds on a carbon basis.

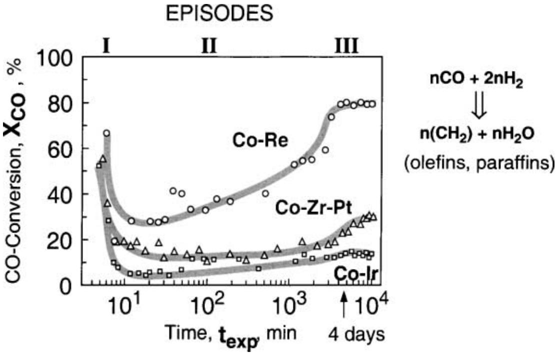


Fig. 1. CO conversion as a function of time ($t_{exp.}$) with three promoted cobalt catalysts at 463 K, 5 bar, $H_2/CO = 1.9$. For further conditions, see Section 2. CO conversion is mainly related to the reaction of chain prolongation (formation of CH_2 and its addition to a surface species for growth).

The results are shown in Fig. 1. From the shape of the curves, three kinetic episodes can be distinguished. During the first ca. 10 min (episode I), the apparent CO conversion decreases drastically as reflecting fast changes due to the delayed build up of the CO partial pressure in the product stream, because of CO retention in the reactor, to fill its void volume and of CO adsorption on the catalyst. In episode II, the CO conversion increases slowly with time to a much higher value from ca. 27 to 80% with the Co–Re-, from ca. 15 to 30% with the Co–Zr–Pt- and ca. 5 to 15% with the Co–Zr-catalysts. It follows that the fresh (well reduced) cobalt catalyst is not much active, however, then in a slow process lasting 3–4 days (episode II), the catalyst generates activity up to an about three times higher level. It is assumed that—as this process is so slow—it involves solid state transformations to perform the “in situ construction” of the FT catalyst.

Comparing the three catalysts, the highest activity was obtained with the rhenium promoted one. However, this result cannot be generalized as it would need further investigations to optimize each catalyst composition and also the procedures and conditions of its preparation and pre-treatment.

3.2. Chain growth and product desorption

The intrinsic feature of FT synthesis is aliphatic chain growth on the catalyst surface. The repeated addition of a monomer is commonly visualized as CH_2

addition. Formation of the main products, α-olefins and paraffins, is then assumed as associative desorption of an alkyl species together with a H-atom or its dissociative desorption via β-H-abstraction.

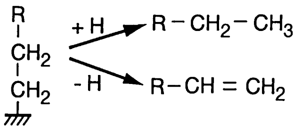


Fig. 2 shows $p_{g,3}$, the chain prolongation probability at carbon number $N_C = 3$ of the growing species, as a function of time (duration of the experiment, $t_{exp.}$) for the experiments with the three catalysts. Growth probability at $N_C = 3$ has been chosen, as at this carbon number, it is the least affected by olefin secondary reactions [8].

It is seen that during the period of "in situ construction" of the catalyst, the selectivity changes towards a much higher growth probability.

Growth or desorption are alternative reaction possibilities of the hydrocarbon chains on the catalyst surface as indicated in Fig. 2 (right). The ratio of these two reaction rates is the same as that of the probabilities of reaction of the respective surface species ($r_g/r_d = p_g/p_d$). The following rate ratios have been taken from Fig. 2.

Catalyst	r_g/r_d at $t_{exp.} = 10$ min	r_g/r_d at $t_{exp.} = 10^4$ min	Factor of increase
Co–Re	2.3	6.1	2.6
Co–Zr	1.3	4.0	3.0
Co–Ir	1.0	3.7	3.7

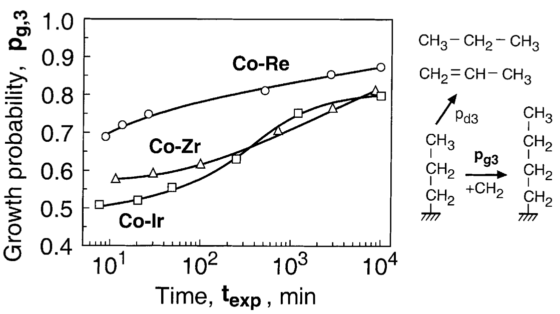


Fig. 2. Growth probability $p_{g,3}$ as a function of time ($t_{exp.}$) with three promoted cobalt catalysts (463 K, 5 bar, $H_2/CO = 1.9$).

These numbers show that the ratio of growth to desorption rates increase with time by a factor of about 3. It is concluded that during catalyst construction—in addition to the FT activity increase—the particular feature of the FT regime is established, the propensity for chain growth, or in other words the "polymerization nature" of FT synthesis. In an earlier publication [9], the specific inhibition of desorption reactions has been defined as characteristic of the FT regime. Correspondingly, it is concluded that a change in the nature of the active sites happens during episode II of early cobalt catalyst life.

Ideal polymerization performance of the FT reaction would imply carbon number independent chain growth probability as representing a horizontal line in the diagram of growth probability as a function of carbon number of the growing species N_C. It is seen in Fig. 3 that there occur distinct deviations from ideality and this particularly occurs in the early stages of an experiment ($t_{exp.} \cong 100$ min):

- low value of p_g at $N_C = 1$ indicating increased methane formation;
- high value of p_g at $N_C = 2$ indicating strong ethene readsorption for chain growth [8];
- increase of p_g with N_C in the range of C_6–C_9, as to be explained by with carbon number increasing olefin-(1) readsorption for further chain growth [8,10].

At steady state ($t_{exp.} = 8620$ min), the ideal (polymerization) behaviour is almost achieved, except for $N_C = 1$, where the low value reflects the additional methane formation. It is concluded that only after restructuring, the active sites of FT synthesis are clearly developed (see the further discussion below).

3.3. Chain branching

The FT CO hydrogenation preferentially produces linear chains of CH_2 groups. In addition, a small extent of methyl branching occurs. Any branching reaction should be assumed to be more demanding in space at the active site than linear chain growth. This would explain the generally observed decrease of branching probability with chain length [7,11], as the chain to be branched becomes more spacious with its length. At $N_C = 4$ of the growing species, branching probability commonly is the highest. This

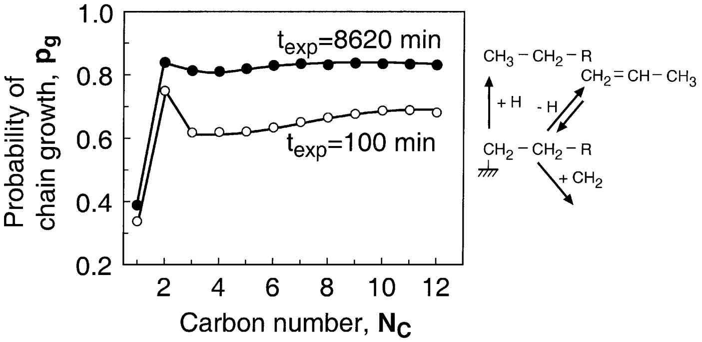


Fig. 3. Growth probability p_g as a function of carbon number N_C at the beginning ($t_{exp.} = 100$ min) and at steady state ($t_{exp.} = 8620$ min) of FT synthesis with the catalyst Co–Zr–SiO$_2$ (463 K, 5 bar, $H_2/CO = 1.9$).

probability, $p_{gbr,4}$, has been chosen to discuss the time dependence of branching probability (Fig. 4). With the Zr- and Ir-promoted catalysts, branching probability is relatively high at the beginning ($p_{gbr,4} = 0.075$ and 0.055, respectively at $t_{exp.} = 15$ min) but declines to 0.03 and 0.015, respectively, within about 10 h ($t_{exp.} = 600$ min). This is interpreted as an increase of spatial constraints at the sites on which chain growth occurs. With the Re-promoted catalyst, branching probability is very low ($p_{gbr,4} = 0.02$) already at the beginning and merely changes with increasing time. Then, this means that the spatial constraints at the sites of chain growth exist from the beginning and the kind of these sites—in contrast to those with the otherwise promoted catalysts—were considered to be the same from the beginning in spite of the high increase of activity with time. At steady state (e.g. $t_{exp.} = 10^4$ min), branching probability is low and almost the same (ca. 2%) with all the three catalysts.

Amazingly at the beginning of the FT experiment, when the branching probability is high (curve for $t_{exp.} = 162$ min in Fig. 5), a principally different shape of the curve of branching probability with dependence on carbon number, as compared with the curve for steady state ($t_{exp.} = 9600$ min), has been obtained. From $N_C = 5$ onwards here, the branching probability increases (not decreases) with carbon number. Thus at the beginning, a different mechanism appears to contribute to chain branching. As at the beginning, the spatial constraints at the FT sites are to be assumed low, then α-olefin readsorption in position 2 can be possible for further chain growth to result in a methyl side group.

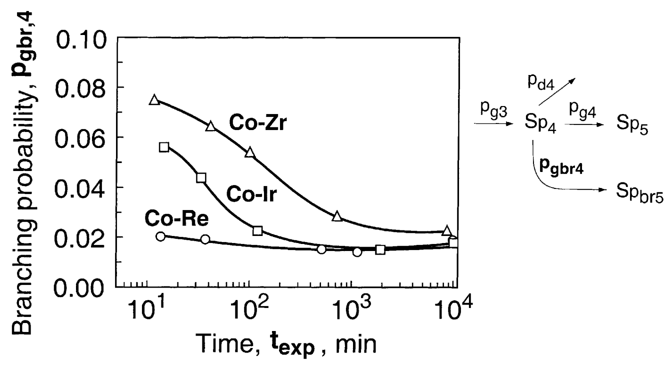


Fig. 4. Branching probability $p_{gbr,4}$ as a function of time ($t_{exp.}$) for three cobalt catalysts (463 K, 5 bar, $H_2/CO = 1.9$).

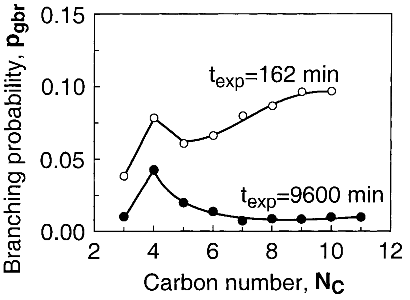
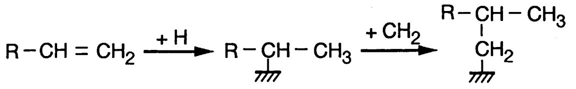


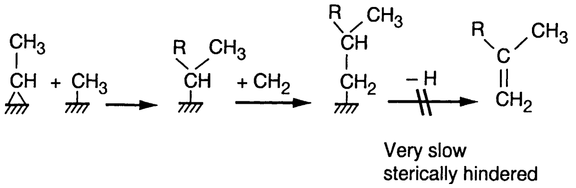
Fig. 5. Branching probability as a function of carbon number N_C at the beginning ($t_{exp.} = 162$ min) and at steady state ($t_{exp.} = 9600$ min) of FT synthesis with the catalyst Co–Zr–SiO$_2$ (463 K, 5 bar, $H_2/CO = 1.9$).



$$R{-}CH{=}CH_2 \xrightarrow{+H} R{-}\underset{\perp}{CH}{-}CH_3 \xrightarrow{+CH_2} \begin{array}{c} R{-}CH{-}CH_3 \\ | \\ \underset{\perp}{CH_2} \end{array}$$

This adsorption should be favoured at increasing size of the olefin molecule. (Under steady state conditions, olefins adsorb on FT sites rather exclusively with the terminal carbon atom, as this readsorption for further chain growth has been observed to be not associated with chain branching [12].)

Remarkably, branching probability is always low for $N_C = 3$, the smallest species where branching is possible. To explain this behaviour, it is recalled that in the kinetic model for calculation of branching probability, the desorption probability for branched and nonbranched species is taken as equal; however, the reaction of desorption as an olefin (the main FT desorption reaction) can be assumed to be strongly spatially demanding at the site in case of a neighboured tertiary C-atom and therefore specifically slow.



3.4. Olefinicity

Among the product olefins of different chain length, those with carbon number 4 appear to be the least affected by secondary reactions [8]. Therefore, the composition of the C$_4$ hydrocarbon product fraction is used for the discussion of olefinicity with dependence on time, $t_{exp.}$ (Fig. 6).

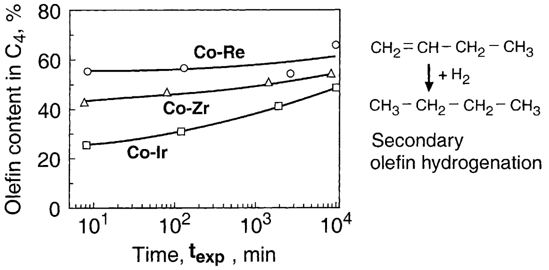


Fig. 6. Olefin content of the C$_4$ fraction of FT products as a function of time ($t_{exp.}$) for three cobalt catalysts (463 K, 5 bar, $H_2/CO = 1.9$).

As the olefin content increases with time, it is concluded that during the catalyst formation period those sites on which secondary hydrogenation occurs disappear. This conclusion will be discussed more deeply below. It is also seen that the differently promoted catalysts show a different time dependence in this aspect. With the Co–Re catalyst from the beginning, the olefin content in the C$_4$ fraction remains almost the same indicating again that with this catalyst—from the beginning—the kind of active sites remains (almost) the same.

Similar conclusions are drawn for the time dependence of secondary double bond shift from Fig. 7 showing the olefin-(1) content among the C$_4$ olefins as a function of time t_{exp}.

3.5. In situ FT catalyst construction

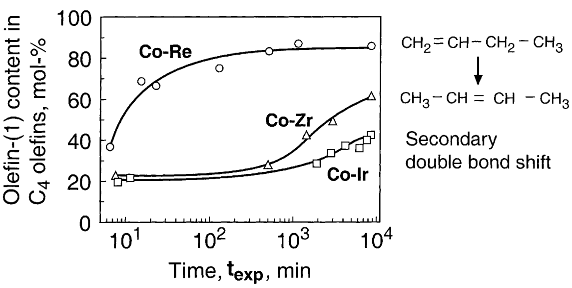


Fig. 7. Olefin-(1) content in the C$_4$ fraction as a function of time ($t_{exp.}$) for three cobalt catalysts (463 K, 5 bar, $H_2/CO = 1.9$).

From the above described development of activity and selectivity with time of cobalt catalysts for FT synthesis, it is concluded that the kinetic regime of FT synthesis is generated slowly under reaction conditions. An in situ construction of the “true FT catalyst” is therefore envisaged.

This “catalyst construction” shall now be considered more profoundly. CO chemisorbs strongly on cobalt (as well as on Ni and Ru) and it has been pointed out by Pichler [13] that FT synthesis performs under conditions not so far from those which allow (thermodynamically) carbonyl formation from these metals. Then the reaction of CO with the metal surface can be assumed to induce surface restructuring in direction to surface enlargement through segregation. Fig. 8 gives a schematic thermodynamic picture of segregation in competition with sintering. Segregation of the surface will be favoured against sintering if the free energy of CO adsorption overcompensates that of reducing the surface area through sintering. Surface segregation can explain the observed activity increase with time, as segregation means an increase of the specific surface area and, respectively, of the number of active sites. Nickel surface segregation by CO adsorption has been reported by Ponec et al. [14]. Images of a cobalt metal surface which had been used for FT synthesis have been obtained by scanning tunnelling electron microscopy by Wilson and de Groot [15]. It is deduced from these pictures that segregation produces an ordered surface structure. The depth of segregation is generally just one atomic layer and the rather uniform distance of the peaks is ca. 30 Å. It follows that by segregation through CO chemisorption, a disproportionation of plane sites happens in sites of low coordination on top positions and sites of high coordination in hole positions.

In the segregated catalyst state, thus three sorts of sites can be visualized:

1. Peak sites and mountain sites of low coordination with several free valences for binding surface species and “ligands”. On these site reactions alike, those known for carbonyl complexes can be assumed and specifically the reaction step of chain growth should be possible.
2. Hole and valley sites of high coordination. These should be suited for CO dissociation.
3. Remaining plane sites with the common activity/specificity of hydrogenation catalysts, however, being much “poisoned” by strong CO chemisorption in the FT regime.

The observed initial changes of selectivity and activity during formation of the FT regime are well explained in consequence of surface site disproportionation as for high and low coordinations.

It has been observed [16] that high performance of cobalt catalysts in FT synthesis was only obtained when during the initial stages of a run the reaction temperature was approached very gradually. This supports the concept of in situ FT catalyst construction

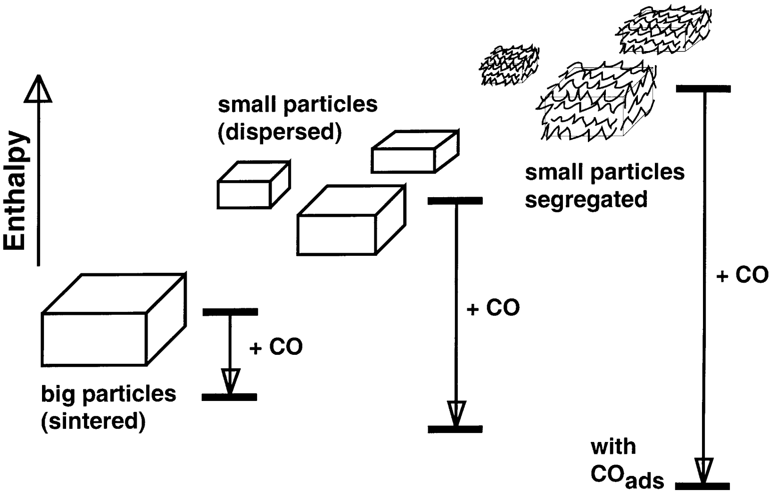
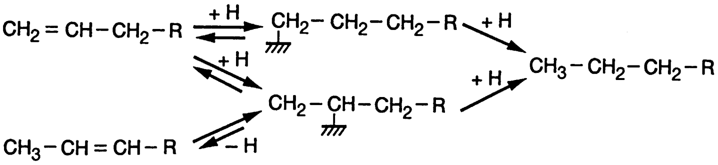


Fig. 8. Thermodynamic view of segregation against sintering of cobalt particles. Specific enthalpy of cobalt as for big crystals: small crystals and segregated small crystals with and without chemisorbed CO.

through segregation which would need sufficient time at favourable conditions: relatively low temperature at relatively high CO partial pressure.

3.6. The FT alkyl grove

The major (primary) products of FT synthesis on cobalt are linear olefins with terminal double bonds (70–80 mol%) and linear paraffins [12]. These compounds are thought to be formed by desorption of alkyl groups: associative desorption for a paraffin molecule and dissociative desorption for an olefin molecule:

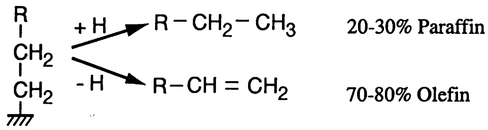


As the desorption probability is—in a first approximation—carbon number independent (except for $N_C = 1$), it follows a similar distribution on carbon numbers of the chemisorbed alkyls as that of the hydrocarbon products. Thus, alkyl species of different chain length bonded to the catalyst surface can be imagined to form a kind of an "alkyl grove". The individual trees of which are soaring into the fluid phase. As the growth probability increases during catalyst formation, the mean height of this grove will increase accordingly. As the number of FT sites increases, simultaneously, the density of the alkyl grove will increase also. Alkyl species should be favourably located on sites of low coordination (on top sites) with distinct complex character, similar to the well known alkyl–carbonyl-complexes in homogeneous catalysis, as pertinent, e.g. in olefin hydroformylation. "Carbonyl surface complexes" have been proposed by Pichler [13] to be of mechanistic importance in FT synthesis.

Remarkably, the olefin desorption probability is higher than that for paraffin [9]. This means that in the FT regime the alkyl species are very stable against desorption as paraffin molecules. Even desorption as olefin is slow as compared with chain prolongation (this is a necessary conclusion for any chain growth to occur) proving again the high stability of alkyl species in the FT regime.

The view that chemisorbed alkyls are particularly stable surface species (intermediates) in FT synthesis is supported by several observations:

1. The reaction of double bond shift has been proposed to perform according to the following kinetic scheme [9]:



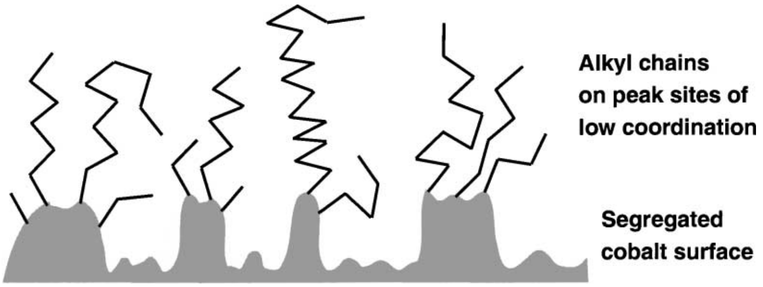


Fig. 9. Principal view of the "living alkyl grove" during FT synthesis on cobalt: alkyl chains are the very stable intermediate species in FT synthesis; their desorption reaction is strongly suppressed; the alkyl chains are preferentially located on cobalt peak sites of low coordination; further, free coordinations may be occupied by "ligands" as CO, CH_2 and others; the "alkyl grove" reaches its steady state after completion of surface restructuring; at steady state, growth and decay of "alkyl trees" are in balance.

Relatively high degrees of double bond shift have been noticed at moderate degrees of hydrogenation [8]. It is concluded that addition of the first H to the olefin is fast and reversible, whereas addition of the second H (associative desorption of the paraffin molecule) is slow and irreversible. Again the alkyl species is seen to be very stable against hydrogenation.

2. At $N_C = 1$, the methyl species cannot form an olefin molecule, and only desorbs associatively with hydrogen to yield methane. Paraffin desorption has been concluded to be particularly slow. Then, this explains the suppression of methane formation (which would be much favoured thermodynamically), a prerequisite for any chain growth reaction to proceed.
3. High stability of methyl species on a palladium catalyst has been reported by Albers et al. [17]. A used catalyst was found to be covered with methyl groups which had even poisoned its

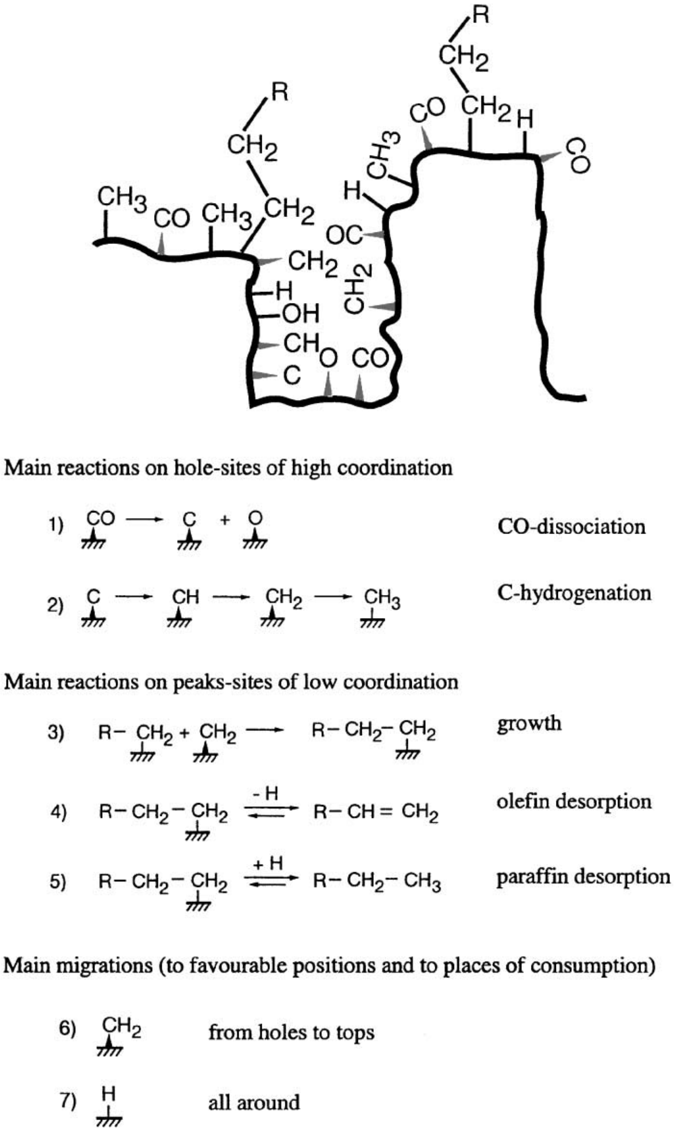


Fig. 10. Schematic picture of surface species on the segregated cobalt surface and main FT reactions.

hydrogenation activity. The methyl species were thought to be located on top positions of the catalyst surface which nicely supports the above conclusion of alkyl chains to be preferentially bonded to peak sites of the segregated catalyst. The method of investigation had been neutron scattering.

4. Characterization of the FT regime with cobalt as the catalyst has also been performed by means of ^{13}CO steady state isotopic transient studies [18] indicating a high relative surface coverage with CO of ca. 70%. The C_1-coverage (e.g. methyl) amounted to 27% and that of C_2^+ to about 1%. Replacement of C_1H_x species was specifically slow as consistent with a high stability of the methyl species.

Generalizing from the several observations and conclusions, a simplified schematic picture of the alkyl grove on the catalyst surface during FT synthesis with cobalt is presented in Fig. 9.

A picture of FT synthesis with the cooperating different cobalt sites is now schematically presented in Fig. 10. Chain growth is related to top sites where reactions, similar to those in homogeneous complex catalysis, are possible. CO dissociation is assumed to perform on sites of high coordination as pertinent for holes and valleys of the surface. Hydrogen is available all around; however, the reaction of H for associative paraffin desorption is seriously suppressed. Collaboration of the different sorts of sites is achieved by migration of particularly CH_2 in direction to top positions.

Remaining plane sites of the Co catalyst are widely poisoned through CO chemisorption, but to some extent still available for minor reactions, as olefin isomerization, olefin hydrogenation and methane formation. Several further reactions are minorily possible. Their relative participation varies during construction of the “true catalyst” and also with changing reaction conditions. Thus these minor reactions are interesting indicators for tracing the kinetic regime on the catalyst surface (as will be objective of a separate communication).

4. Summary

Changes of reaction rate and selectivity in the initial stages of FT synthesis have been investigated with three promoted catalysts. Reaction rate increased by about a factor of 3 and selectivity changed towards higher chain growth probability and lower branching probability. As these changes are only slow, they appear to indicate a catalyst restructuring process. The details of selectivity changes are used to characterize the changes of the nature of the active sites.

This FT cobalt catalyst “in situ construction” is addressed as surface segregation through strong CO chemisorption as supported from complementary literature. By this process, the number of sites increases largely and the sites disproportionate into sites of higher and lower coordinations on the expense of plane sites. The on top sites of low coordination allow for reactions similar to those known from homogeneous complex catalysis and the sites of low coordination (in holes and valleys) preferentially give CO dissociation.

It follows from the selectivity studies, but also neutron scattering on used hydrogenation catalysts, that alkyl species are particularly stable intermediates. Due to the observation/conclusion that the reaction of associative paraffin desorption, the combination of an alkyl with a H is particularly slow in the FT regime, a kind of “alkyl grove” is imagined to exist on the surface of the operating FT catalyst.

Then the steady state kinetic regime of FT synthesis with cobalt (and Ni and Ru) is understood as established during an initial process of self-organization in which the catalyst surface is segregated to produce the true collaborating FT sites of high and low coordinations and a steady state “alkyl grove” on the catalyst surface, whereas the reactions on common hydrogenation sites (plane sites) are seriously poisoned (through strong CO chemisorption).

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