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REGULARITIES OF SELECTIVITY AS A KEY FOR DISCRIMINATING FT-SURFACE REACTIONS AND FORMATION OF THE DYNAMIC SYSTEM

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Primary product compositions from FT-CO-hydrogenation have been obtained. A kinetic model has been used to calculate rate constants, rates and probabilities of the elemental surface reactions as a function of carbon number from product composition data. Formation of the catalytic system in the initial stage of an experiment is characterized by selectivity changes as related to elemental surface reactions.

1. Introduction

The complexity of product composition in FT-CO-hydrogenation is regarded as a source of information about surface reactions involved and the nature of the catalyst under dynamic conditions. In order to obtain kinetic data on the elemental surface reactions within the mechanism of product formation, a kinetic scheme has to be modelled. The first quantitative model of chain growth by Herington [1] in 1946 respected the grossly exponential decline of moles of product compounds with increase of their carbon number. Anderson and Friedel in 1950 [2] extended the model to the formation of methyl-branched molecules. The model has been developed mathematically in more detail for quantitative description of product compositions by Wojciechowski et al. in 1983 [3,4]. Abstract kinetic parameters were introduced in order to reduce the complexity of mathematical treatment. Pichler, Schulz and Elstner in 1967 [5] inspected the Anderson-assumption of carbon number independent chain growth probability via capillary GC of various products and found appreciable deviations.

A general kinetic model of surface reactions in FT-CO-hydrogenation using simply rate constants, rates and probabilities for individual elemental types of surface reactions as parameters was established by Schulz, Erich and Beck in 1987 [6–8]. This model is very flexibel and particularly suited to calculate individual kinetic constants for elemental surface reactions and thus to prove the validity of the simplified assumptions from detailed product composition data. It is suited as well to discriminate primary product compositions from those which are obscured by secondary reactions. It has already been used to determine the variation of kinetic constants of the elemental reactions linear growth, branching and formation of paraffins and olefins as a function of chain length, reaction parameters and catalysts properties for a few cases. Additional work is needed to compile such data for broader ranges of stationary conditions, materials and also the instationary phases of establishing the catalytic FT-system.

2. Experimental

Experimental data are given in table 1. The reactors used were of the fixed bed and the CSTR-slurry-phase type. The fixed bed version is suited for investigation of transient systems as existing in the initial stage of experiments. The continous, ideally mixed slurry phase reactor with finely divided catalyst, suspended in squalane as a solvent resembles that which has been used by Satterfield et al. [9]. It is well suited for isothermal kinetic studies. Catalysts were prepared via precipitation. Individual reaction conditions are reported below along with the

Table 1
Experimental data for performing the CO-hydrogenation and determining product compositions differentially

EXPERIMENTAL

Reactors
- fixed bed
- continous–ideally mixed–slurry phase

Catalysts: precipitated
- $Fe\text{-}Mn\text{-}K_2O$
- $Fe\text{-}Cu\text{-}K_2O$

Reaction parameters
- temperature: 250, 310 °C
- pressure: 5–20 bar
- Time on stream

Product sampling
- instantaneous (duration $< 1/10$ sec)
- of the hot (250 °C) gas/vapour-product stream representative composition C_1 to C_{17}

Quantitative evaluation
- neopentane internal standard for organic compounds
- nitrogen internal standard for inorganic gases

ANALYSIS

- high resolution GC $C_1 - C_{20}$
- product composition grouped according to compound type and carbon number

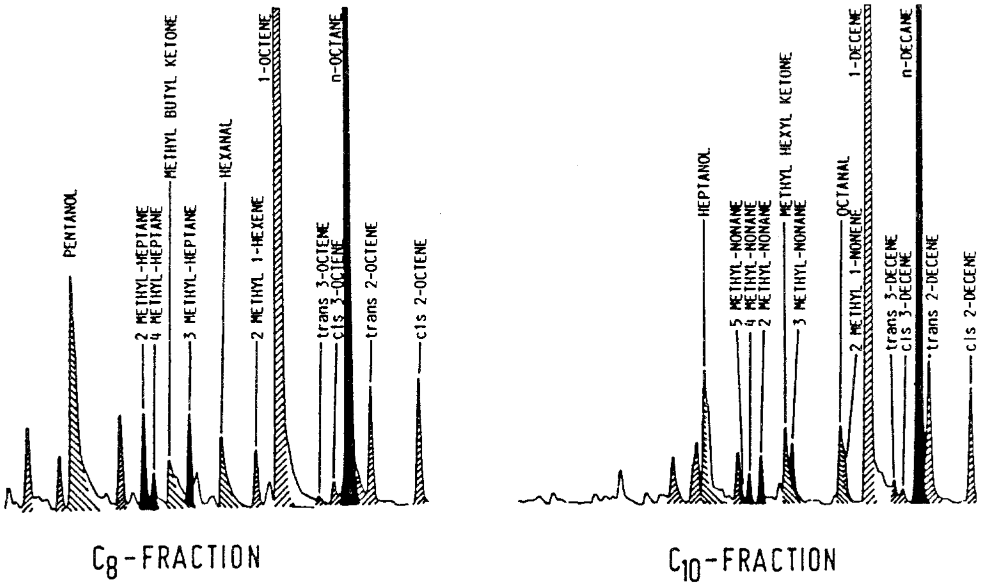


Fig. 1. Sections C_8 and C_{10} of a FT-product chromatogram (CSTR-reactor, catalyst 100; Fe:3 Cu:2 K_2O:37 Al_2O_3, 250 °C, $p_{CO} = 2.5$ bar, $p_{H_2} = 10$ bar).

respective results. Time on stream changes of activity, selectivity and carbon deposition in the early stages of experiments were measured through instantaneous gas/vapour-sampling in small glas ampoules, application of high resolution GC and reference compounds for quantitative evaluation. Fig. 1 shows the product fractions C_8 and C_{10} of a typical chromatogram.

3. Results and discussion

IDEAL AND REAL KINETIC SCHEMES AND MODELS

Common features of product composition from FT-synthesis and from homogeneous polymerization have stimulated people to regard FT-synthesis as a polymerization reaction also. This view is certainly part of the truth, because there is no doubt presently, that chain growth in FT-synthesis proceeds via a repeated addition of a C_1-species. However, the FT-growth of the aliphatic chain by only one CH_2-group necessarily comprises at least 11 elemental steps of surface reactions:

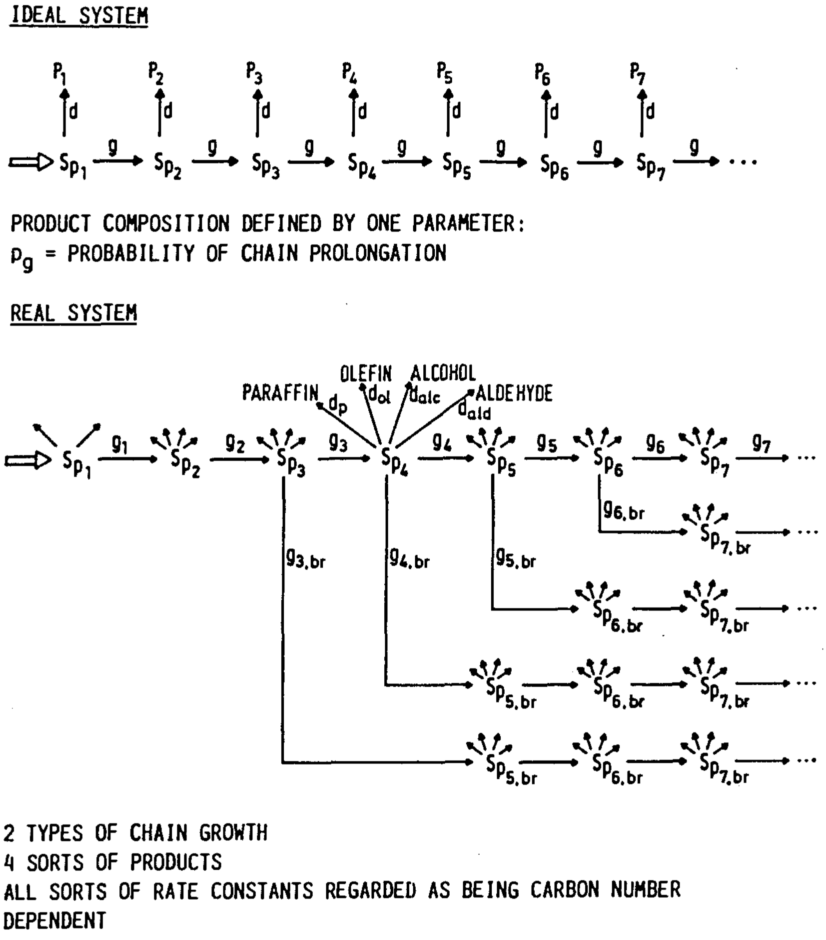
- Chemisorption of CO
- Formation of 4 chemisorbed H
- Splitting of the C/O-bond
- Formation of a new C/C-bond
- Transfer of 2 H to the carbon atom
- Transfer of 2 H to the oxygen atom.

Therefore Ft-chain growth is a very unique example of “Chemistry in Two Dimensions”. To remind this, the term “non trivial surface polymerization” has been proposed [8]. There are additional non-polymerization-like characteristics of FT-systems:

- addition of the C_1-species is also possible to the penultimate C-atom of the chain
- at least 4 sorts of products can be obtained simultaneously: paraffins, olefins, alcohols and aldehydes.

Furtheron secondary reactions proceed more or less in FT-systems as there are

- olefin hydrogenation
- double bond shift
- hydroformylation of olefins
- hydrogenolysis of olefins
- incorporation of small olefins in growing chains.


IDEAL SYSTEM

PRODUCT COMPOSITION DEFINED BY ONE PARAMETER:
p_g = PROBABILITY OF CHAIN PROLONGATION

REAL SYSTEM

2 TYPES OF CHAIN GROWTH
4 SORTS OF PRODUCTS
ALL SORTS OF RATE CONSTANTS REGARDED AS BEING CARBON NUMBER DEPENDENT

Fig. 2. “Ideal” and “real” kinetic scheme of Fischer-Tropsch chain growth [8].

The concept of this work is to establish FT-systems which yield primary products, the compositions of which reflect the FT-surface chemistry and with the help of the kinetic model, to evaluate kinetic data as reaction rates and probabilities and rate constants for elemental reaction steps.

Fig. 2 gives the "ideal" and the "real" model of FT-chain growth and product formation. The ideal model describes the total product composition with the value of only one parameter, the chain prolongation probability (p_g). In the real model two types of chain growth (linearly, branchedly) and 4 sorts of product formation (paraffin, olefin, alcohol, aldehyde) are admitted and all 6 types of reaction constants are suspected to be carbon number dependent. Now from measured detailed product compositions the values of e.g. probability of the individual reactions are calculated. The idea is, thus to obtain a deeper understanding of the surface reactions and to use this for development of catalysts and desired selectivities.

TRANSIENT FT-SYSTEMS IN THE INITIAL STAGE OF CONVERSION

H. Pichler et al. quoted in 1940 that the reaction conditions of FT-synthesis are nearby to those of the formation of carbonyls from the catalytically active metals (Fe, Co, Ni, Ru) [10]. This corresponds to a very strong associative chemisorption of CO under conditions of FT-synthesis which is probably accompanied by a reconstruction of the catalyst surface in the beginning of an experiment. During the FT-synthesis on iron catalysts, carbon is deposited on the surface and reacts to several iron carbids in addition to the formation of a graphitic carbon phase [11]. It follows again, that the catalyst undergoes major changes in the beginning of an experiment. This transient instationary period of synthesis has been investigated for the differential amounts of carbon deposition and activity and selectivity changes by Schulz, Bamberger and Gorre in 1984 [12]. New results of this kind are presented in fig. 3 for FT-synthesis on a Fe-Mn-K_2O catalyst at 250 and at 310 °C. The yield of organic compounds was determined in the reactor effluent and this is a measure of catalyst activity. It is seen, that not the freshly reduced catalyst is the most active. Initially e.g. after 10 minutes, the activity is still very low (~ 3% yield of hydrocarbons) and only after ca. 1000 minutes (~ 17 hours) a stationary activity (~ 20% yield of hydrocarbons) is obtained. The difference of the total of carbon is gaseous products to 100% relates to the sum of carbon deposited on the catalyst, yield of wax remaining on the catalyst and losses. In the first 30 minutes this difference is relatively high and is rapidly declining. It corresponds majorily to carbon deposition on the surface and reaction of this carbon with near-to-surface-catalyst-atoms. Within the next 1000 minutes only a slow decreasing carbon deposition (decreasing difference in carbon balance from ca. 10 to ca. 6%) occurs (wax selectivity is estimated to about 15%; wax yield will increase with time on stream in this range of experiment). Slow carbon deposition from 30 to 1000 minutes time on stream is

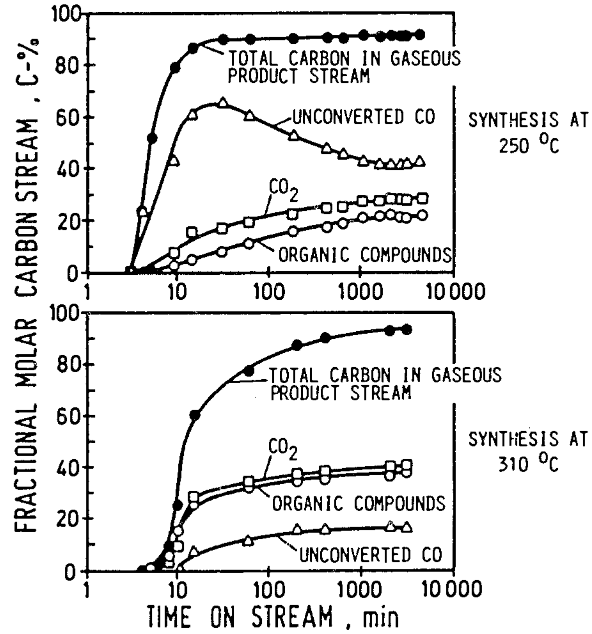


Fig. 3. FT-hydrogenation in the initial stage of experiment. Fractional molar carbon streams in the reactor effluent as a function of time on stream. (Catalyst 100 Fe : 279 Mn : 12.4 K_2O, $p = 10$ bar, $H_2/CO = 2$; reduced with H_2 at 350 °C.)

associated with the major activity development (HC yield increases from ca. 5 to ca. 20%).

At 310 °C reaction temperature (lower diagram in fig. 3) again the two phases of catalyst reconstruction can be distinguished, however they appear in a shorter time. The first rapid reconstruction period ends already after 15 minutes. The second deep reconstruction period consumes much more carbon. Quasi stationary activity (ca. 30% yield of hydrocarbons) is obtained already after ca. 200 minutes. With respect to the catalytic system it can also be concluded, that the active Fischer-Tropsch sites are only formed during initial stage of the experiment. Their number and nature will depend on the experimental conditions.

Change of selectivity with time on stream for the same experiments as in fig. 3 is shown in fig. 4. At 250 °C the probability of chain growth is observed to be as low as 40% after about 7 minutes time on stream. It soon increases to ca. 65% after 10 minutes and remains almost constant. The fraction of ethylene in C_2 characterizes secondary olefin hydrogenation. It attains a value of 80% after about 100 minutes time on stream. The α-olefin in the fraction of olefins C_4 is constant and 95% after 10 minutes. In this system stationary selectivity is achieved earlier (ca. 100 minutes) than stationary activity (ca. 1000 minutes, compare figs. 3 and 4) and it may be concluded that after 100 minutes only the number of sites increases whereas their nature remains the same.

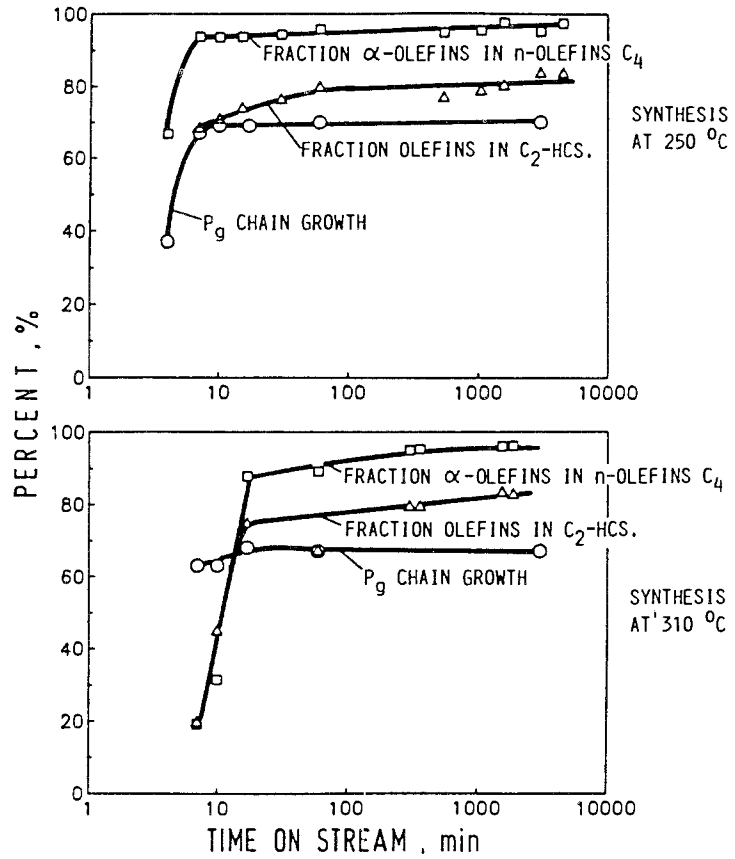
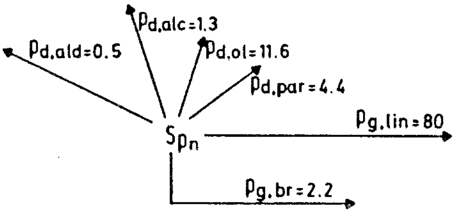


Fig. 4. Change of selectivity in the initial stage of FT-hydrogenation (conditions as in fig. 3).

Table 2
Conclusion: mechanistic role of aldehydes and alcohols

1) In most FT-systems secondary conversion of aldehydes and alcohols obscures their role in the FT-reaction mechanism.
2) FT-products with primary composition of aldehydes and alcohols have been obtained with Fe-Mn-K_2O catalysts. The molar logarithmic distributions show parallel lines for linear aldehydes and linear alcohols. This proves the primary nature of aldehydes and alcohols, because secondary reactions do yield different distributions which are not polymerization-like.
3) The molar logarithmic distributions of aldehydes and alcohols are parallel lines to those of linear hydrocarbons, indicating their formation through the same intermediates.
4) For the investigated system the following values of reaction probabilities of a chemisorbed intermediate of carbon number $N = 8$ (S_{p_n}) were obtained (values given in %)



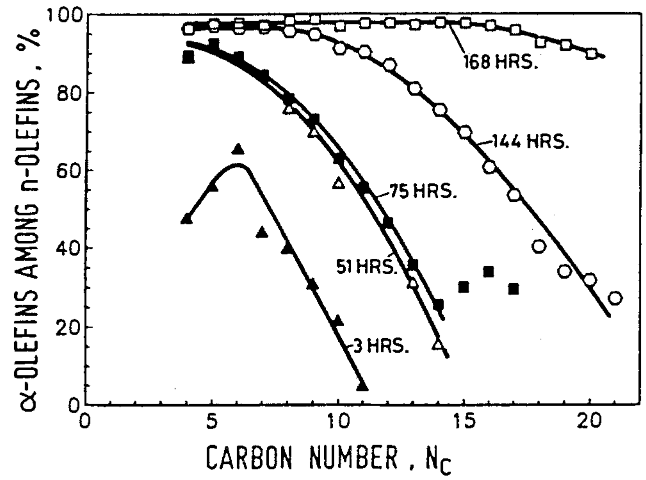


Fig. 5. Influence of reaction time on α-olefin selectivity, defined as content of α-olefins in n-olefin fractions (100 Fe:551 Mn:24 K_2O, 250 ° C, 10 bar, $H_2/CO = 1.9$, GHSV = 500 h^{-1}).

At 310 ° C reaction temperature similar tendencies are to be seen, however stationary selectivity is obtained slowlier. This is explained with a generally higher rate of secondary reactions at elevated temperature.

α-olefin selectivity evaluated as the content of α-olefins within the fraction of n-olefins is reported as a function of the carbon number with the reaction time as parameter for another catalyst system with higher manganese content in fig. 5. Here the change of selectivity continues more than 150 hours and only after 168 hours an about 95% selectivity of α-olefins was obtained.

ALDEHYDES AND ALCOHOLS AS PRIMARY FT-PRODUCTS

Alcohols and aldehydes are known as byproducts of FT-CO-hydrogenation. The mechanistic implication of their formation is not safely proven until today. Results of product composition obtained with an iron manganese catalyst are

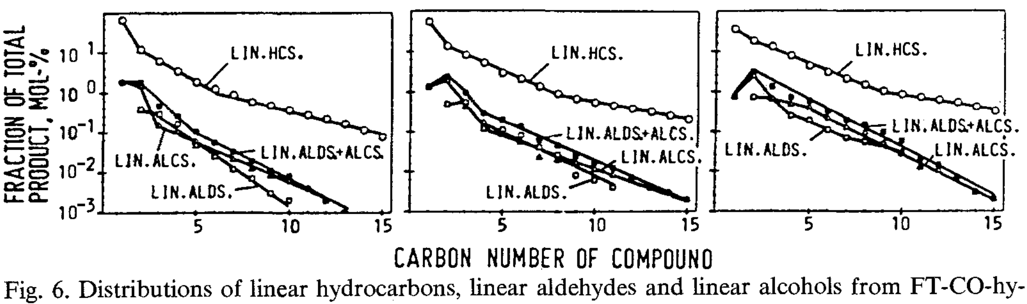


Fig. 6. Distributions of linear hydrocarbons, linear aldehydes and linear alcohols from FT-CO-hydrogenation after 6, 22 and 129 hours time on stream. (Catalyst 100 Fe:510 Mn:24.5 K_2O; 250 ° C; $H_2/CO = 1.92$; 10 bar; GHSV = 500 h^{-1}.)

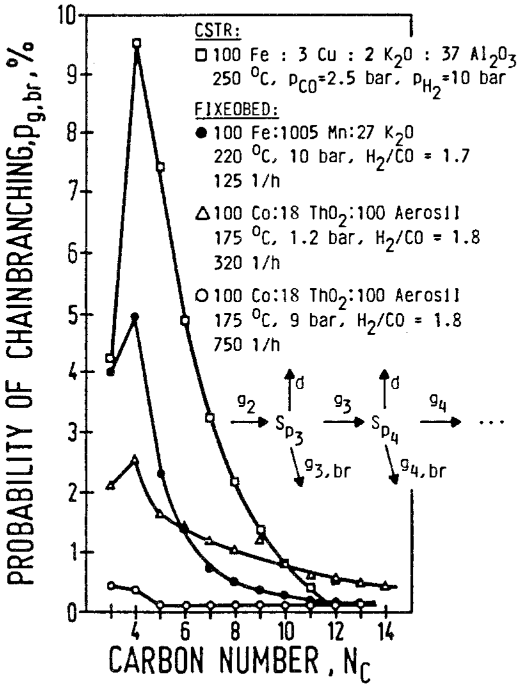


Fig. 7. Chain branching as a function of carbon number.

shown in fig. 6 for 6, 22 and 129 hours of time on stream. It is observed that the slope of the curves for linear hydrocarbons in the range C_2 to ca. C_7 is approximately the same as that of the sum of alcohols and aldehydes. With increasing time on stream there develops a region C_4 to C_7 in which the curves for alcohols and aldehydes are parallel. Thus, it is concluded that alcohols and aldehydes are both primary products of FT-CO-hydrogenation. The conclusions for these experiments are summarized in table 2 which also shows the relative reactions rates of a Fischer-Tropsch surface species with $N_C = 8$ (S_{p_8}). The values of these reaction rates are equal to those of reaction probability (p):

- linear chain growth-$p_{\text{g lin}}$ = 80%
- branched chain growth $p_{\text{g br}}$ = 2.2%

Table 3
Conclusion: chain branching

1) Probability of chain branching is seen to be strongly dependent on carbon number
2) An exponential decline from the second possible step is observed for major range of conditions
3) The first step of branching is governed by separate rules
4) Branching probability is regarded as a measure of degree of demanding spacious restriction at the active sites because any imaginable branching reaction will need more space than linear chain growth

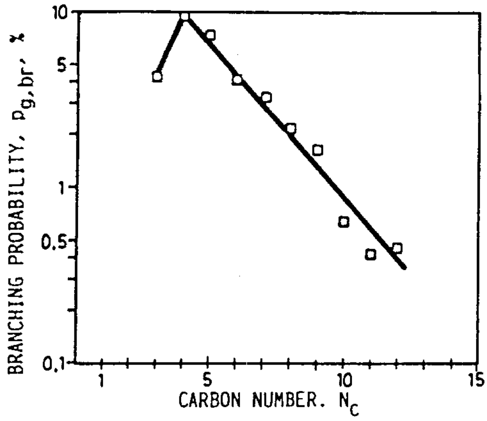


Fig. 8. Logarithmic graph of branching probability as a function of carbon number. (100 Fe: 3 Cu : 2 K_2O : 37 Al_2O_3, 250 °C, $p_{CO} = 2.5$ bar, $p_{H_2} = 10$ bar, CSTR-reactor).

- formation of olefin $p_{d\,ol} = 11.6\%$
- formation of paraffin $p_{d\,par} = 4.4\%$
- formation of alcohol $p_{d\,alc} = 1.3\%$
- formation of aldehyde $p_{d\,ald} = 0.5\%$

CHAIN BRANCHING

With the help of the "real model" in fig. 2 and the simplifying assumptions of only one sort of products and carbon number independent rate constants for chain prolongation the results of chain branching probability as a function of carbon number are shown in fig. 7. One of these curves is also presented as a semilogarithmic diagram (fig. 8). This proves the exponential decline of branching probability with increasing carbon number (except for the first step). Conclusions for chain branching are summarized in table 3.

4. General conclusion

Evaluation of reaction probabilities of surface species on the basis of detailed product composition data and a "real kinetic model" of surface reactions has provided new understanding of the nature of elemental reactions and the catalyst active sites. The dynamic nature of the system is illustrated by differential measurements of mass balances and selectivity in the initial stage of experiments. Further systems shall be evaluated on the basis of the methods described here.

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