STUDIES ON THE FUNDAMENTAL REACTIONS OF THE FISCHER-TROPSCH SYNTHESIS FROM REACTION BALANCES

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SUMMARY

It is shown by means of examples from literature and from our investigations, that hydrogenation hydrogen for the reduction of primary olefines originates from two different sources. For iron-catalysts, the hydrogenation-hydrogen is exclusively obtained by an additional shift towards carbon-dioxide-reaction. For cobalt- and ruthenium-catalysts, such shift also occurs at higher temperatures, but, however, in most of these cases, hydrogenation-hydrogen results from direct activation. Still more frequently, the hydrogenation-hydrogen is made available from both these sources.

It is also shown, by means of some balance calculations, that the different reaction-stages occur according to full number relationship, and a number of such cases is discussed.

The occurrence of negative \((x-f)\)-values in some special cases and its cause are discussed in detail. It is found that this is caused by an additional consumption of CO beyond the normal reduction reactions. Synthesis conditions for the occurrence of negative \((x-f)\)-values are investigated for cobalt- and iron-catalysts. It is observed that the additional consumption of CO is preferably found at low temperatures and low \(H_2:CO\)-gas ratios, and is due to the occurrence of such intermediate reactions, which under normal reaction conditions do not contribute to the products, but become visible only under the condition, where the final reactions are retarded. Such reactions are found to be carbonyl-formation, carbide-formation, carbon-deposition, oxo-reaction and subsequent aldehyde reduction, and direct methanol-formation, apart from olefine and paraffin formation. An extended scheme has been presented which includes these intermediate reactions in addition to final reactions. Synthesis examples have been calculated according to this scheme, and their results are discussed.

INTRODUCTION

In our previous publications the possibilities of the application of the reaction balances to get a clear idea of the involved reactions have been discussed. A
simple scheme of calculation has been presented to calculate the amounts of olefine and paraffin fractions separately from gas analytical data only which further enables one to predict the distribution of the products and their build-up. These investigations present the calculations of hydrogenation-hydrogen and the formulation of polymerisation function based on the formation of intermediate radicals. It could be shown that at a certain stage, the reaction occurs as a radical polymerisation, and a part of the olefinic primary products are converted into paraffins by hydrogenation. It was further found that with all the catalysts, preferably iron catalysts and also to a certain extent with cobalt and ruthenium catalysts, two radical forming reactions, the water-reaction (a-reaction) and carbon-dioxide-reaction (b-reaction) are occurring simultaneously. The latter reaction was found to be responsible in many cases for the availability of hydrogenation hydrogen.

Investigations on the Origin of Hydrogenation-Hydrogen.—Most of the gas analytical data, available from literature, have been calculated, according to our reaction scheme, the main values have been tabulated and subdivided according to the types of catalysts, as well as according to the reported reaction conditions. We have thus calculated from literature 32 cobalt catalysts, normal pressure; 49 cobalt catalysts, medium pressure; 51 iron catalysts, medium pressure, and 55 ruthenium catalysts high pressure examples. In addition to these, we have carried out, about 50 experiments with cobalt catalyst and about 20 with iron catalyst, under certain limiting reaction conditions, and these are also evaluated and tabulated. As it is not possible to present here all our voluminous data, we have presented the most important relationships in the Figs. 1, 2 and 3.

In the first instance, the values of carbon dioxide-reaction (b-values) have been plotted against the hydrogenation-hydrogen \((x - f)\)-values, as shown in Fig. 1. From this figure, one can arrive at the following conclusions:

1. All the points for cobalt and ruthenium catalysts are found to be crowded in the lower part of the positive side of \((x - f)\)-axis, but on both sides of \(b\)-axis.

2. All the points for iron catalysts occupy preferably the middle part of the diagram and are found around the \(b\)-value of about 16.666. They are however, more scattered and less restricted within a certain area.

3. In some few cases, however, negative \((x - f)\)-values are found which are also plotted in Fig. 1. The significance of these negative values will be discussed in detail in this paper.

4. Some cases of small negative \(b\)-values are certainly identical with \(b\)-values = zero, as nowhere reduction of \(\text{CO}_2\) is to be anticipated what would be indicated hereby.

5. In the case of cobalt and ruthenium catalysts, it is often observed that for relatively high \((x - f)\)-values, the \(b\)-values are low, and also low \(b\)-values are obtained at relatively small \((x - f)\)-values, including \((x - f) = 0\).
Fig. 1. $b/(x - f)$-Plots for Co-, Ru- and Fe-Catalysts.

$\bigcirc = \text{Co-Catalysts, Normal Pressure.}$  $\triangle = \text{Ru-Catalysts, High Pressure.}$

$\bullet = \text{Co-Catalysts, Medium Pressure.}$  $\bigcirc = \text{Fe-Catalysts, Medium Pressure.}$
Fig. 2. $b/(x - f)$-Dependency for Co-, Ru- and Fe-Catalysts.

- $\bigcirc$: Co-Catalysts, Normal Pressure.
- $\bigtriangleup$: Ru-Catalysts, High Pressure.
- $\bullet$: Co-Catalysts, Medium Pressure.
- $\ast$: Fe-Catalysts, Medium Pressure.
Fig. 3. Representation of Usage-(ρ)- and Reduction-(ρₐ)-Ratios of Co-, Ru-, and Fe-Catalysts with Change in Hydrogenation-Hydrogen-(x - f)-Values.


One can observe that all the (x - f)-values in the case of iron catalysts, as developed in our earlier publications, result from an additional shift towards b-reaction, in addition to b₀-reaction the magnitude of which has been indicated as bₙ. The following equations have been found valid:—
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\[ b = b_0 + b_n \]

(1)

and

\[ (x - f) = 3b_n \]

(2)

and also,

\[ \frac{2a + b + (x - f)}{a + 2b} = \frac{2a_0 + b_0}{a_0 + 2b_0} = p. \]

(3)

The validity of these equations can be ascertained from the straight lines which can be drawn in all the cases through the respective points between \( b_0 \)-values for \( (x - f) = 0 \) and respective \( b \)-values. All these lines have the slope of 3.0 (vide Fig. 2). From this it is clearly observed that the increase in \( (x - f) \)-value while keeping the original usage ratio of \( \text{H}_2 \) to \( \text{CO} \) for \( a \)- and \( b \)-reactions is always connected with a respective shift from \( a \)-reaction to \( b \)-reaction of the order of \( b_n \)-value.

For Co- and Ru-catalysts, however, there exist two different possibilities. A number of reactions runs in the same way as described for iron catalysts. The \( b_0 \)-value is positive, even for the limiting case of \( (x - f) = 0 \), or may be just zero also. All of the hydrogenation-hydrogen in these cases is also obtained by a respective shift from \( a \)- to \( b \)-reaction of \( b_n \), just as is common with iron catalysts. A large number of these examples, however, give negative \( b_0 \)-values. This would indicate that all or part of the hydrogenation-hydrogen has been directly activated, and is not obtained by a shift to \( b \)-reaction. This type of hydrogenation-hydrogen is obviously directly activated by the catalyst, under the conditions where it is unable to activate the respective \( b \)-reaction. We are of the opinion that this direct activation of hydrogenation-hydrogen occurs in some direct connection with \( a \)-reaction. The same Co- and Ru-catalysts can further activate hydrogenation-hydrogen in both the ways, as can be seen from a number of cases from Figs. 1 and 2. This is always the case where there is a positive \( b \)-value, but a negative \( b_0 \)-value. The part of the hydrogenation-hydrogen which lies on the negative side of the \( b \)-axis (dotted lines in Fig. 2) is directly activated, and the other part which is situated above the \((x - f)\)-axis from \( b = 0 \) onwards, is activated by \( b \)-reaction. It is interesting to note that complete or partial direct activation of hydrogenation-hydrogen occurs with catalysts commonly known as highly hydrogen-active. It is not as yet known whether these different types of hydrogenation-hydrogen which can be classified as \((x - f)_a \) and \((x - f)_b \), react differently or cause different product compositions. However, it is often observed that a full number relationship exists between the two.

In the course of calculations of a large number of quite different examples, it was found that the \((x - f)\)- and also \( a \)- and \( b \)-values are almost close to full numbers or give full numbers when multiplied by 3.0 (vide Figs. 1 and 2). This would definitely indicate that within the reaction scheme, the different single reactions occur according to full number relationships which is to be expected from molecular ratios and that these different reactions are also subdivided among
themselves accordingly. This phenomenon will be shown along with other findings in case of some typical examples later.

From some of these examples which show very low positive values of \((x - f)\) or which gives \((x-f)\)-values equal to zero, the product composition according to groups of olefines, paraffins and oxygenated compounds, could be obtained. It is found that with decrease in \((x - f)\)-value, there is an increase in oxygenated compounds, and further the products become more high molecular and richer in olefinic compounds.

A few typical examples of the different types, discussed above, are presented in the form of their reaction balances:

No. 1.—Synthesis with Co-catalyst, Example No. 209: positive \((x - f)\)-value, exclusively obtained by \(b\)-reaction; \(b_0\)-value = zero or nearly zero or positive.

\[
(x - f) = 3.079 \quad b > b_0 \quad (x - f)_a = 0.000 \quad H_2/CO = 1.29
\]
\[
b_0 = 0.004 \quad b_\infty = b - b_0 \quad (x - f)_b = 3.079 \quad \rho = 2.00
\]
\[
b = 1.031 = 1.027 \quad (x - f) = 3.079
\]

**Balance:**

\[
31.276 \text{ CO} + 62.552 \text{ H}_2 = 31.276 (\text{CH}_2) + 31.276 \text{ H}_2\text{O}
\]
\[
0.008 \text{ CO} + 0.004 \text{ H}_2 = 0.004 (\text{CH}_2) + 0.004 \text{ CO}_2
\]
\[
2.054 \text{ CO} + 1.027 \text{ H}_2 = 1.027 (\text{CH}_2) + 1.027 \text{ CO}_2
\]

\[
33.338 \text{ CO} + 63.583 \text{ H}_2 = 32.307 (\text{CH}_2) + 31.276 \text{ H}_2\text{O} + 1.031 \text{ CO}_2
\]
\[
+ 3.079 \text{ H}_2 = 3.079 \text{ H}_2
\]

\[
33.338 \text{ CO} + 66.662 \text{ H}_2 = 100.000 \text{ CO} + \text{ H}_2
\]

No. 2.—Synthesis with Co-catalyst, Example No. 210: positive \((x - f)\)-value, exclusively obtained by direct activation; negative \(b_0\)-value; \(b = 0\) or very small positive or negative value.

\[
(x - f) = 9.263 \quad b > b_0 \quad (x - f)_a = 9.020 \quad H_2/CO = 2.25
\]
\[
b_0 = -3.007 \quad b_\infty = b - b_0 \quad (x - f)_b = 0.243 \quad \rho = 2.297
\]
\[
b = 0.081 = 3.088 \quad (x - f) = 9.263
\]
Balance:

\[ 30.165 \text{ CO} + 60.330 \text{ H}_2 = 30.165 \text{ (CH}_2\text{)} + 30.165 \text{ H}_2\text{O} \]
\[ 0.162 \text{ CO} + 0.081 \text{ H}_2 = 0.081 \text{ (CH}_2\text{)} + 0.081 \text{ CO}_2 \]

\[ 30.327 \text{ CO} + 60.411 \text{ H}_2 = 30.246 \text{ (CH}_2\text{)} + 30.165 \text{ H}_2\text{O} + 0.081 \text{ CO}_2 \]
\[ + 0.243 \text{ H}_2 = 0.243 \text{ H}_2 = (x - f)_b \]
\[ + 9.020 \text{ H}_2 = 9.020 \text{ H}_2 = (x - f)_a \]
\[ + 9.263 \text{ H}_2 = 9.263 \text{ H}_2 = (x - f') \]

\[ 30.327 \text{ CO} + 69.674 \text{ H}_2 = 100.000 \text{ CO} + \text{H}_2 \]

This balance can also be written as follows in case we use the \(a_0\)- and \(b_0\)-values only:

\[ 36.340 \text{ CO} + 72.680 \text{ H}_2 = 36.340 \text{ (CH}_2\text{)} + 36.340 \text{ H}_2\text{O} \]
\[ - 6.014 \text{ CO} - 3.007 \text{ H}_2 = -3.007 \text{ (CH}_2\text{)} - 3.007 \text{ CO}_2 \]

\[ 30.326 \text{ CO} + 69.673 \text{ H}_2 = 33.333 \text{ (CH}_2\text{)} + 36.340 \text{ H}_2\text{O} - 3.007 \text{ CO}_2 \]

If this catalyst would have been able to activate hydrogenation-hydrogen with the aid of \(b\)-reaction, then it should have behaved as follows:

Balance:

\[ 28.823 \text{ CO} + 57.645 \text{ H}_2 = 28.823 \text{ (CH}_2\text{)} + 28.823 \text{ H}_2\text{O} \]
\[ 3.007 \text{ CO} + 1.504 \text{ H}_2 = 1.504 \text{ (CH}_2\text{)} + 1.504 \text{ CO}_2 \]

\[ 31.830 \text{ CO} + 59.149 \text{ H}_2 = 30.327 \text{ (CH}_2\text{)} + 28.823 \text{ H}_2\text{O} + 1.504 \text{ CO}_2 \]
\[ 3.007 \text{ CO} + 1.504 \text{ H}_2 = 1.504 \text{ (CH}_2\text{)} + 1.504 \text{ CO}_2 \]

\[ 34.837 \text{ CO} + 60.653 \text{ H}_2 = 31.831 \text{ (CH}_2\text{)} + 28.823 \text{ H}_2\text{O} + 3.008 \text{ CO}_2 \]
\[ + 4.512 \text{ H}_2 = 4.512 \text{ H}_2 \]

\[ 34.837 \text{ CO} + 65.165 \text{ H}_2 = 100.002 \text{ CO} + \text{H}_2 \]
The unit which is underlying the performance of this catalyst is obviously equal to 1.504. The catalyst is not in a position to combine 4 units of CO with 2 units of H₂, according to $b$-reaction (total 6 units). Instead, it activates 1 unit of CO with 2 units of H₂ according to $a$-reaction (total 3 units). Hence 3 more units are then available as hydrogen for hydrogenation. It means that under given conditions, it could not activate $4 - 1 = 3$ units CO. However, instead it could activate the same number of units of H₂ although for another purpose, i.e., hydrogenation.

No. 3.—Synthesis with Co-catalyst, Example No. 101: positive $(x - f)$-value, resulting from two sources, directly activated as well as from $b$-reaction; negative $b_0$-value; positive $b$-value.

\[
\begin{align*}
(x - f) &= 6.944 \quad b > b_0 \\
\quad (x - f)_a &= 1.944 \quad \text{H}_2/\text{CO} = 2.023 \\
b_0 &= -0.649 \quad b_n = b - b_0 \\
(x - f)_b &= 5.000 \quad \rho = 2.060 \\
b &= 1.666 \quad = 2.315 \\
\frac{(x - f)}{ \text{H}_2} &= 6.944
\end{align*}
\]

Balance:

\[
\begin{align*}
29.353 \text{ CO} + 58.706 \text{ H}_2 &= 29.353 (\text{CH}_2) + 29.353 \text{ H}_2\text{O} \\
3.333 \text{ CO} + 1.666 \text{ H}_2 &= 1.666 (\text{CH}_2) + 1.666 \text{ CO}_2
\end{align*}
\]

\[
\begin{align*}
32.686 \text{ CO} + 67.316 \text{ H}_2 &= 31.019 (\text{CH}_2) + 9.353 \text{ H}_2\text{O} + 1.666 \text{ CO}_2 \\
+ 5.000 \text{ H}_2 &= 5.000 \text{ H}_2 = (x - f)_b \\
+ 1.944 \text{ H}_2 &= 1.944 \text{ H}_2 = (x - f)_a \\
6.944 \text{ H}_2 &= 6.944 \text{ H}_2 = (x - f)
\end{align*}
\]

\[
\begin{align*}
32.686 \text{ CO} + 67.316 \text{ H}_2 &= 100.002 \text{ CO} + \text{ H}_2
\end{align*}
\]

According to $a_0$- and $b_0$-conditions, the following balance would have to be written:

Balance:

\[
\begin{align*}
33.982 \text{ CO} + 67.964 \text{ H}_2 &= 33.98 \text{ (CH}_2) + 33.982 \text{ H}_2\text{O} \\
- 1.298 \text{ CO} - 0.649 \text{ H}_2 &= -0.649 \text{ CH}_2) - 0.649 \text{ CO}_2
\end{align*}
\]

\[
\begin{align*}
32.684 \text{ CO} + 67.316 \text{ H}_2 &= 100.000 \text{ CO} + \text{ H}_2
\end{align*}
\]
If the catalyst would have been worked under such conditions that the original reaction consumption would have been carried out, then the following balance should have been found.

**Balance:**

\[
\begin{align*}
31 \cdot 386 \text{ CO} &+ 62 \cdot 772 \text{ H}_2 = 31 \cdot 386 \text{ (CH}_2) + 31 \cdot 386 \text{ H}_2\text{O} \\
1 \cdot 298 \text{ CO} &+ 0 \cdot 649 \text{ H}_2 = 0 \cdot 649 \text{ (CH}_2) + 0 \cdot 649 \text{ CO}_2
\end{align*}
\]

\[
\begin{align*}
32 \cdot 684 \text{ CO} &+ 63 \cdot 421 \text{ H}_2 = 32 \cdot 035 \text{ (CH}_2) + 31 \cdot 386 \text{ H}_2\text{O} + 0 \cdot 649 \text{ CO}_2 \\
0 \cdot 649 \text{ CO} &+ 1 \cdot 298 \text{ H}_2 = 0 \cdot 649 \text{ (CH}_2) + 0 \cdot 649 \text{ H}_2\text{O}
\end{align*}
\]

\[
\begin{align*}
33 \cdot 333 \text{ CO} &+ 64 \cdot 719 \text{ H}_2 = 32 \cdot 684 \text{ (CH}_2) + 32 \cdot 035 \text{ H}_2\text{O} + 0 \cdot 649 \text{ CO}_2 \\
&+ 1 \cdot 947 \text{ H}_2 = 1 \cdot 947 \text{ H}_2
\end{align*}
\]

\[
\begin{align*}
33 \cdot 333 \text{ CO} &+ 66 \cdot 666 \text{ H}_2 = 100 \cdot 000 \text{ CO} + \text{H}_2
\end{align*}
\]

This means that only 1 \cdot 947 (2.00 approx.) hydrogenation-hydrogen would have been made available, if the catalyst could have activated b-reaction up to the limit of \(b_0\)-value, whereby the total b-reaction would have come to \(b_0 + b\). But as the catalyst was not able to activate the \(b_0\)-part, it was in a position to activate 3 times the quantity of \(\text{H}_2\) for hydrogenation instead. We further observe that the ratio between the two hydrogenation-hydrogen amounts is remarkable according to full numbers, namely, 5:2. Already here one can see that \(\text{H}_2\) and CO can replace each other and can be used either in \(a\)- or \(b\)-reaction, according to different reaction conditions.

No. 4—Synthesis with Iron catalyst, Example No. 440: positive \((x - f)\)-value; positive \(b_0\)-value and positive \(b\)-value; \((x - f)\) comes from \(b_\pi\)-reaction.

\[
(x - f) = 4 \cdot 054 \quad b > b_0 \quad \text{H}_2/\text{CO} = 1 \cdot 061
\]

\[
b_0 = 17 \cdot 978 \quad \rho = 0 \cdot 949
\]

\[
b = 19 \cdot 329 \quad b_\pi = b - b_0 = 1 \cdot 351
\]

**Balance:**

\[
\begin{align*}
12 \cdot 653 \text{ CO} &+ 25 \cdot 306 \text{ H}_2 = 12 \cdot 653 \text{ (CH}_2) + 12 \cdot 653 \text{ H}_2\text{O} \\
35 \cdot 956 \text{ CO} &+ 17 \cdot 978 \text{ H}_2 = 17 \cdot 978 \text{ (CH}_2) + 17 \cdot 978 \text{ CO}_2 \\
2 \cdot 702 \text{ CO} &+ 1 \cdot 351 \text{ H}_2 = 1 \cdot 351 \text{ (CH}_2) + 1 \cdot 351 \text{ CO}_2
\end{align*}
\]

\[
\begin{align*}
38 \cdot 658 \text{ CO} &+ 19 \cdot 329 \text{ H}_2 = 19 \cdot 329 \text{ (CH}_2) + 19 \cdot 329 \text{ CO}_2 \\
51 \cdot 311 \text{ CO} &+ 44 \cdot 635 \text{ H}_2 = 30 \cdot 982 \text{ (CH}_2) + 12 \cdot 653 \text{ H}_2\text{O} + 19 \cdot 329 \text{ CO}_2 \\
&+ 4 \cdot 054 \text{ H}_2 = 4 \cdot 054 \text{ H}_2
\end{align*}
\]

\[
\begin{align*}
51 \cdot 311 \text{ CO} &+ 48 \cdot 689 \text{ H}_2 = 100 \cdot 000 \text{ CO} + \text{H}_2
\end{align*}
\]
All ruthenium catalysts, investigated by us, react in a similar way as the Co-catalyst and therefore, no special ruthenium catalyst example is given here.

The interdependence of the reactions among themselves as shown here and the significance of the origin of hydrogenation-hydrogen in this connection, can be further clarified by plotting $H_2:CO$ usage ratios against hydrogenation-hydrogen, as shown in Fig. 3. In this figure we have plotted $\rho$ and $\rho_*$ values defined as

$$\rho = \frac{2a + b + (x - f)}{a + 2b}$$

and

$$\rho_* = \frac{2a + b}{a + 2b}$$

Again, here the catalysts form the two distinct groups according to their usage ratios, the Co- and Ru-catalysts having a ratio in the neighbourhood of 2:1, and Fe-catalysts having a ratio around 1:1. The limiting curves, shown in this figure, represent exclusive types of $(x - f)$-activation. For instance, the upper curve $G_1$ represents all such cases where $(x - f)$ has been obtained by direct activation only, while the lower curve $G_2$ represents the cases where $(x - f)$ has been activated by $b_n$-reaction only. All values lying between these two curves have both types of activation of hydrogenation-hydrogen.

For Fe-catalysts such limiting curves can be obtained for every $\rho$-value, down to 0.5. For the values of $\rho = 1.5$ and 1.0, the respective limiting curves $G_3$ and $G_4$ have been drawn.

Investigations on the Existence of further Intermediate Reactions.—During the calculation of many synthesis examples, according to the method presented earlier, it was found, that in a limited number of cases negative $(x - f)$-values are obtained when the equation

$$(x - f) = (2a + b + x - f) - 2 (a + 2b) - 3b$$

was used. These negative values are generally found in the cases of Co- and Ru-catalysts, where low temperatures and low $H_2:CO$-ratios in the synthesis gas are offered to them, and in the case of Fe-catalysts, at high temperatures and at normal pressure. This can be taken in the first instance, as an indication of the occurrence of certain other distinct reactions, not yet included in our earlier simplified reaction scheme. Some such examples of negative $(x - f)$-values have also been included in Figs. 1, 2 and 3. As negative $(x - f)$-values are not possible, distinct deviations from the normal reaction course leading to hydro-carbon-formation must have occurred.

If more detailed investigations into the causes possible for such negative $(x - f)$-values are carried out, it can be easily seen that such negative values will always result when the second term of the right side in equation (6) becomes relatively large and the first and the third terms become smaller. Such changes will only
result when more CO has been consumed, than can be accounted for by CO₂-
reaction or by H₂O-reaction, which will require more hydrogen. This means that
an increase of the second term in equation (6) can neither be due to a- nor
b-value, as then also the other terms should increase. From this it can be con-
cluded that an additional quantity of CO has reacted in one or several ways, as yet
unknown, and not accounted for in our reaction scheme.

Further in such cases of negative \((x - f)\)-values, \((x - f)\)-value cannot be
obtained from the other derived equation

\[
(x - f) = 100 - 3(a + b),
\]

as in most of all the reported cases in literature the \(a\)-value is not obtained analyti-
cally, but has been calculated from the value of \((a + 2b)\), obtained from C-balance
calculations. If now the term \((a + 2b)\) should contain such other additional CO
quantities which are not accounted for either by CO₂-reaction or H₂O-reaction,
then the value of \(a\) can no more be calculated, but must be estimated experimentally.
It is therefore necessary to estimate separately the value of \(a\), in all further exper-
imental work of this type. Since sometime we, therefore, carried out all our experi-
ments, wherein the amount of water formed was estimated, apart from the equally
important CO₂-value available from gas analysis. By using these values of \(a\) and \(b\)
in equation (7), we can get an experimentally supported \((x - f)\)-value, for all
such cases where no other side reactions occur. In all these cases, including those
where other side reactions take place, we will also get positive \((x - f)\)-values, but
these values will no more be pure hydrogen values, but will include such other
CO and H₂-values, which are consumed for side reactions.

We have studied the occurrence of such intermediate reactions and purposely
established such synthesis conditions, as extremely low temperatures and low
synthesis gas H₂:CO-ratios and also normal pressure conditions, under which such
intermediate reaction-stages become stabilized. It appears that under such reaction
conditions, the reduction reactions \(a\) and \(b\) are no more sufficiently accelerated.
as the result of which the intermediate reactions which, under normal conditions.
have been too slow compared with the reduction-reactions, to be recognised, have
now become relatively faster so that their products remain unchanged to a certain
extent.

The evaluation of balances of synthesis experiments carried out under these
conditions has revealed that the following reactions are existing and result in the
formation of stable products:

1. Reaction of CO and H₂ with radicals or olefines formed from the reduction
   and subsequent polymerisation reactions, in place of hydrogenation-hydrogen.
   Here we come across a "direct oxo-reaction". This reaction will consume CO
   and H₂ in the ratio 1:1 and the products will be aldehydes.

2. Reduction of aldehydes, formed by direct oxo-reaction, into alcohols.
   Here one more equivalent H₂ is consumed, which is also a part of total hydrogenu-
tion-hydrogen. Oxo- and reduction reactions together consume CO and H₂ in the ratio 1:2, similar to a-reaction. However, no water is being formed.

(3) Direct formation of methanol by \(1 \text{CO} + 2 \text{H}_2\). Also here the ratio is the same as for a-reaction, however again no water is formed.

(4) The disappearance of CO on the catalyst, where it is initially bound by activated adsorption and further used in carbonyl formation.

If these carbonyls are not continuously removed from the catalyst surface by consecutive reactions, like reduction reactions, it is observed that the catalyst is quickly deactivated. The part of CO which is used for carbonyl formation neither uses H₂ nor forms CO₂ and can therefore be measured as residual quantity only. Our experiments indicate that for all the catalysts carbonyl formation is the first fundamental stage in the Fischer-Tropsch-synthesis after activated adsorption. Carbonyls may then further react either with H₂ to form radicals and water, or with each other to form CO₂ and carbides which on further reduction by H₂ will give radicals.

(5) The formation of stable carbides leads to the deposition of carbon on the catalyst. This part of CO does not use any hydrogen but forms CO₂.

The occurrence of reactions under (1) and (2) and also (3) to some extent is very common with Fe-catalysts and seems to run parallel with activation of hydrogenation-hydrogen. These reactions are responsible for the formation of oxygenated compounds and are indicated by negative \((x - j)\)-values following our former scheme. The more important reaction considered as the key reaction for the whole scheme is the one described under (4), i.e., carbonyl-formation, and perhaps also the reaction under (3).

In order to include these reactions in the simplified reaction scheme, proposed earlier, it is necessary to extend this scheme, as some or all of the intermediate reaction products appear in the final products under such conditions, as outlined here. This becomes necessary in order to obtain quantitative results also for such cases. The extended scheme can be written as follows:

### Extended Reaction Scheme

\[
\begin{align*}
\text{Water reaction} & \quad a \text{CO} + 2a \text{H}_2 = a (\text{CH})_2 + a \text{H}_2\text{O} \quad (8) \\
\text{Carbon dioxide reaction} & \quad 2b \text{CO} + b \text{H}_2 = b (\text{CH}_2) + b \text{CO}_2 \quad (9) \\
\text{Carbide formation} & \quad 2c \text{CO} = c \text{C} + c \text{CO}_2 \quad (10) \\
\text{Radical polymerisation} & \quad (a + b)(\text{CH}_2) = x(\text{CH}_2)n \quad (11) \\
\text{Methanol formation} & \quad x(\text{CH}_2)n = f(\text{CH}_2)q + g(\text{CH}_3)p + (x - f - g) \text{H}_2 \quad (12) \\
\text{Paraffin formation} & \quad s \text{CO} + 2s \text{H}_2 = s(\text{CH}_3\text{OH}) \quad (13) \\
\text{Water reaction} & \quad (x - f - g)(\text{CH}_2)q + (x - f - g) \text{H}_2 = (x - f - g)([\text{CH}_2]q + \text{H}_2) \quad (14)
\end{align*}
\]
Studies on Fundamental Reactions of Fischer-Tropsch Synthesis

\[ g \left( \text{CH}_2 \right)_r + g \text{CO} + g \text{H}_2 = g \left[ \left( \text{CH}_2 \right)_r + \text{CO} + \text{H}_2 \right] \]

Oxo-reaction

\[ g \left[ \left( \text{CH}_2 \right)_r + \text{CO} + \text{H}_2 \right] + g \text{H}_2 = g \left[ \left( \text{CH}_2 \right)_r + \text{CO} + 2\text{H}_2 \right] \]

Aldehyde reduction

\[ \text{CO} + \text{Catalyst} = \text{CO} \text{(Catalyst)} \]

Carbonyl formation

\[(a + 2b + 2c + g + s + l) \text{CO} + (2a + b + (x - f - g) + 2g + 2s) \text{H}_2 = f \left[ \text{CO} \right]_q + (x - f - g) \left[ \left( \text{CH}_2 \right)_p + \text{H}_2 \right] + g \left[ \left( \text{CH}_2 \right)_r + \text{CO} + 2\text{H}_2 \right] + s \left( \text{CH}_3\text{OH} \right) + a \text{H}_2\text{O} + (b + c) \text{CO}_2 + c \text{C} + l \left( \text{CO} \text{Cat.} \right) \]

If we now take into consideration only the left part of the equation (18) and relate it to 100% CO + H\(_2\) conversion and exclude the symbols for gases, we obtain an extended equation for hydrogenation-hydrogen:

\[(x - f - g) = 100 - 3(a + b + g + s) - 2c - l \]

In this equation we have to deal with a number of unknowns like, \((x - f - g)\), \(b, c, g, s\) and \(l\). Formerly we have been able to assess \(a\)- and \(b\)-values from C-balance, but now we must try to find out additional unknowns in our investigations. For this a number of possibilities are at our disposal. First we can use the following two equations the data for which can be obtained from C-balance:

\[ \Sigma \text{CO} = a + 2(b + c) + g + l + s \]

(20)

and

\[ \Sigma \text{H}_2 = 2(a + g + s) + b + (x - f - g) \]

(21)

The values for \(a\) and \((b + c)\) are obtained from gas analysis. From the equations (20) and (21) separate values for \((a + g + s)\) and \(l\) can be obtained, if the value for \((x - f - g)\) is known, and in case there is no carbon deposition. The value for \((g + s)\) can be obtained whenever \(a\) is known by separate estimation. Further, we have to take the \(t\)-values (saturates) from gas analysis as almost identical with \((x - f - g)\)-value. This value may not be absolutely identical with hydrogenation-hydrogen value in all the cases, but it will be approximately equal to it, especially in those cases where preferably lighter hydrocarbons are produced. Also when the value for \((x - f - g)\) is low, there is very often the possibility of \((x - f - g)\) and \(t\) having identical values. In Fig. 4, the \(t\)-values for a number of cases of different catalysts are plotted against \((x - f - g)\), and from this figure we can notice the validity of our statement. In case the values for \(t\) and \((x - f - g)\) are not identical, the values for \(l\) will be somewhat too low, if the value for \(t\) is used as hydrogenation-hydrogen value. The number of unknowns reduces to four, when the value for \(t\) is used. It is necessary to point out that, in such cases, the exact evaluation of \((x - f - g)\)-values is no more foremost important, compared to the evaluation of \((g + s)\) and \(l\). It is further observed, through these calculations,
Fig. 4. Proportionality between Hydrogenation-Hydrogen \((x-f)\)-Values and Values of Paraffin-Fractions \((i)\) in Gas Analyses of Fischer-Tropsch Syntheses.

- \(\circ\) = Co-Catalysts, Normal Pressure.
- \(\triangle\) = Ru-Catalysts, High Pressure.
- \(\bullet\) = Co-Catalysts, Medium Pressure.
- \(\oplus\) = Fe-Catalysts, Medium Pressure.

that the carbon deposition is indicated by negative values for \((a + g + s)\) or \((g + s)\) itself. This means that \((a + g + s)\)- or \((g + s)\)-values should be considered as zero and consequently the \(l\) and \(c\) values become measurable. Uptil now we have always found that negative \(a\)- or \((a + g + s)\)-values are the condition for C-deposition, and \textit{vice versa}. Carbon deposition excludes the formation of higher alcohols, and prominence of \(a\)-reaction. The calculation procedure has therefore to be carried out in the following way. From equation (20), a value for \(l\) can be calculated by obtaining the value for \((a + g + s)\) from equation (21) by substituting \(l\) for \((x-f-g)\). If the value \((a + g + s)\), obtained from equation (21), is positive, it will indicate that there is no C-deposition, and then we can obtain the values for \(l\) and \((g + s)\) separately. If \((a + g + s)\)-value is found to be negative, it should
be taken as zero, and then we get the values for \( l \) and \( c \) separately from equation (20). In all such cases where no separate estimation of water formed \((a)\) is made, a sum of \((a + g + s)\) will be obtained as both water reaction and oxo-reaction, followed by aldehyde-reduction, or direct methanol-formation, consume \( H_2 \) and CO in the ratio 2:1, with the only difference, that in the latter reactions no water is formed, but alcohols instead.

The development of such calculations will be shown by two examples, one for cobalt- and other for iron-catalyst. Both the catalysts are operated under the conditions by which the intermediate reactions become prominent.

Experiment No. 186.—Co-catalyst; 150° C., normal pressure; \( H_2/CO \) in synthesis gas = 0.813; \( a = 12.027; (b + c) = 1.295; b = 1.295 - c; t = 2.913 = (x - f - g); \Sigma CO = 62.184; \Sigma H_2 = 37.816; \; H_2/CO = 0.813; \; \rho = 0.608.

In this case there is no possibility of carbon deposit, as the temperature is very low and also \( CO_2 \)-formation is very small, and, therefore, \( c \) can be taken as zero. As the value for \( a \) has been estimated separately, the following calculations for \( l \) and \( (g + s) \) can be made:

\[
\begin{align*}
\frac{\Sigma CO - \Sigma H_2 - 3b + t}{2} &= 2 \times 62.184 - 37.816 - 3 \times 1.295 + 2.913 \\
&= 42.790 CO \\
(g + s) &= \Sigma CO - a - 2b - l = 62.184 - 12.027 - 2 \times 1.295 \\
&= 4.777 CO
\end{align*}
\]

The total reaction can then be balanced as follows:

**Balance:**

\[
\begin{align*}
12.027 CO + 24.054 H_2 &= 12.027 (CH_2) + 12.027 H_2O \\
2.590 CO + 1.295 H_2 &= 1.295 (CH_2) + 1.295 CO_2
\end{align*}
\]

\[
\begin{align*}
14.617 CO + 25.349 H_2 &= 13.322 (CH_2) + 12.027 H_2O + 1.295 CO_2 \\
+ 2.913 H_2 &= 2.913 H_2 & \text{Hydrogenation-hydroger} \\
4.777 CO + 4.777 H_2 &= \text{Oxo-reaction } } + \text{ Methanol } \\
+ 4.777 H_2 &= \text{Aldehyde reduction } } + \text{ formation } \\
42.790 CO &= \text{Carbonyl formation}
\end{align*}
\]

\[
62.184 CO + 37.816 H_2 = 100.000 CO + H_2
\]

Here we come across a very high value for \( l, i.e., \) carbonyl-formation, which is generally found under these conditions. As a result of these carbonyl-depositions,
the catalyst becomes quickly inactivated. In cases of using a synthesis gas with higher $H_2$:CO ratio, but otherwise equally low temperature, the $l$-value is found to be much smaller. Methanol- and higher alcohol-formation cannot be separated unless methanol is separately measured.

**Experiment No. 319.**—Fe-catalyst; 220°C, normal pressure, synthesis gas $H_2$:CO ratio = 0.955; $a = 8.433$; $(b + c) = 23.005$; $b = 23.005 - c$; $t = 1.651 = (x - f - g)$; $\Sigma CO = 63.614$; $\Sigma H_2 = 36.386$; $H_2/CO = 0.955$; $p = 0.572$.

In this case, initially none of the possible main and intermediate reactions can be excluded. The following calculations are necessary:

$$
(g + s) = \Sigma CO - a - 2(b + c) - l = 63.614 - 8.433 - 2(23.005) - l = 9.171 - l
$$

$$
2a + 23.005 - c + t + 2(9.171) - 2l = \Sigma H_2
$$

$$
2l + c = 16.866 + 23.005 + 1.651 + 18.342 - 36.386 = 23.478
$$

$$
(g + s + l) = 9.171
$$

$$
(c + 2l) = 23.478
$$

Considering $(g + s)$, $l$ and $c$ in turn as zero, we find that a valid balance is obtained only when $(g + s)$ is taken as zero. This would indicate that carbon deposition has occurred which automatically excludes alcohol formation. This result is to be expected on account of high temperature and normal pressure, when the reduction and hydrogenation activity of the iron-catalyst, normally already low, is further reduced. For the condition $(g + s) = 0$, we then find

$$
b = \Sigma H_2 - 2a - t = 36.386 - 16.866 - 1.651 = 17.869;
$$

$$
l = 9.171;
$$

$$
c = 23.478 - 9.171 \times 2 = 5.136.
$$

All the reactions can then be balanced as follows:

**Balance:**

$$
8.433 \text{ CO} + 16.866 \text{ H}_2 = 8.433 \text{ (CH}_2\text{)} + 8.433 \text{ H}_2\text{O} + 17.869 \text{ CO}_2
$$

$$
35.738 \text{ CO} + 17.869 \text{ H}_2 = 17.869 \text{ (CH}_2\text{)}
$$

$$
44.171 \text{ CO} + 34.735 \text{ H}_2 = 26.302 \text{ (CH}_2\text{)} + 8.433 \text{ H}_2\text{O} + 17.869 \text{ CO}_2
$$

$$
+ 1.651 \text{ H}_2 = 1.651 \text{ H}_2\text{ Hydrogenation}
$$

$$
44.171 \text{ CO} + 36.386 \text{ H}_2 = 26.302 \text{ (CH}_2\text{)} + 8.433 \text{ H}_2\text{O} + 17.869 \text{ CO}_2
$$

$$
10.272 \text{ CO} = 5.136 \text{ C} + 5.136 \text{ CO}_2\text{ Carbon deposition}
$$

$$
54.443 \text{ CO} + 36.386 \text{ H}_2 = 26.302 \text{ (CH}_2\text{)} + 8.433 \text{ H}_2\text{O} + 17.869 \text{ CO}_2
$$

$$
+ 5.136 \text{ C}
$$

$$
9.171 \text{ CO} = 9.171 \text{ CO}\text{ Carbonyl formation}
$$

$$
63.614 \text{ CO} + 36.386 \text{ H}_2 = 100.000 \text{ CO} + \text{ H}_2
$$
Also in this case, the catalyst becomes quickly inactive due to carbonylisation and C-deposition.

CONCLUSIONS

It is found that under these conditions, when the final reactions in the Fischer-Tropsch synthesis are retarded below the rate of the intermediate reactions, leading to the formation of the final products of paraffins, olefins and oxygenated compounds, the products of the intermediate reactions become more prominent in the final products. Reaction-conditions for such cases for cobalt catalysts are low temperatures and low $\text{H}_2: \text{CO}$ ratio in the synthesis gas, either at normal or medium pressure, and for iron catalysts, similar conditions preferably at normal pressure. The catalyst composition will also direct towards greater stability of products of these intermediate reactions.

Further it is interesting to observe that carbonyl-formation or activated CO-adsorption, seems to be common for both types of catalysts, however, carbonyl-deposition seems to exclude the formation of oxygenated compounds. Therefore, we are of the opinion that the first reaction that could occur is the activated adsorption of CO (apart from the activated adsorption of $\text{H}_2$), which leads to intermediate carbonyl-formation. In the case of hydrogen-active catalysts like Co and Ru, the carbonyl-formation is followed by reduction-reaction, preferably according to water-reaction. To a certain extent, depending upon conditions, as soon as sufficient radicals or olefins are formed, oxo-reaction and subsequent aldehyde-reduction will take place in addition to simultaneous reduction of olefins. Another possibility which we are not yet able to signify with regard to priority, is the intermediate formation of methanol. This reaction definitely occurs by reduction of carbonyls with hydrogen. Whether subsequently methanol is partly reduced into CH$_2$-radicals and water has still to be ascertained. At this stage we cannot say whether methanol is an intermediate product on the way to olefine- and paraffin-formation. In the case of less hydrogen-active catalysts like Fe, the carbonyls may react preferably according to carbon dioxide reaction, into the formation of labile carbides which will then be reduced to radicals and polymerise into olefins. Oxo-synthesis, alcohol-formation and hydrogenation may then occur in the same way as that of Co- and Ru-catalysts. As this carbide scheme will require higher temperatures, permanent C-deposition will be more likely. The $\alpha$-reaction and the oxo-reaction being closely associated, should have similar mechanisms. A complete scheme of the reactions is presented in Fig. 5.

The results presented here so far need further confirmation by experiments of long durations, yielding larger quantities of liquid products. All our findings at present are based, exclusively on gas analytical data and do not include liquid products analysis except $\text{H}_2\text{O}$-formation. The presence of Co- and Fe-carbonyls has been however actually detected in the exit gas, by decomposing the carbonyls at 600° C., and obtaining thereby the metal deposition.
Fig. 5. Reaction Scheme for Fischer-Tropsch Synthesis, including Intermediate Stages.

REFERENCES


REFERENCES FOR EXAMPLES

Example No. 209 .. Lurgi, medium pressure synthesis with water-gas, no recycle, one stage.

Example No. 210 .. Lurgi, medium pressure synthesis with normal synthesis gas, no recycle, one stage.
<table>
<thead>
<tr>
<th>Example No.</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>101</td>
<td>Works Schwarzheide, normal pressure synthesis 1941, one stage.</td>
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<tr>
<td>440</td>
<td>Lurgi, sintered catalyst, 225°C, 20 atmospheres, recycle ratio 3:1.</td>
</tr>
<tr>
<td>186</td>
<td>Own investigations with own catalysts.</td>
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