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Development of ideas concerning the mechanism of the Fischer–Tropsch synthesis

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ABSTRACT. The principal stages in the development of ideas concerning the mechanism of the Fischer–Tropsch synthesis and its modifications are examined and the available literature data about the synthesis are surveyed. Attention has been concentrated on the analysis of modern ideas concerning the mechanism of the interaction of CO and H_2 on the basis of the latest advances in metal complex catalysis. The possibility of the existence of the postulated intermediates and of the occurrence of suggested elementary steps has been demonstrated in relation to model organometallic systems.

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I. Introduction

At the beginning of the 20th century Sabatier[1] and then Fischer and Tropsch[2,3] first achieved the catalytic synthesis of organic compounds from CO and H_2. Apart from the synthesis of methane[1] and aliphatic hydrocarbons, mainly having the normal structure,[2,3] from the synthesis gas (a mixture of CO and H_2), during the last decades other organic compounds have been synthesised, including methanol,[4] lower alkanes,[5] polymethylenes,[6] isoalkanes,[7] olefins,[8] high alcohols,[9] acids,[10,11] and polyols.[12] With the exception of certain compounds such as acetylene and formaldehyde, there are no thermodynamic limitations to the preparation of a wide range of organic products by this procedure.[13]

At the present time the term Fischer–Tropsch synthesis is given to the set of reactions involving the direct conversion of CO + H_2 into a mixture of aliphatic hydrocarbons and oxygen-containing compounds in which the number of carbon atoms ranges from two upwards. Typical catalysts of these reactions are Ni, Co, Fe, and Ru.[14,15] Under certain conditions, the predominating products of the conversion of the synthesis gas are oxygen-containing compounds in the presence of iron catalysts and hydrocarbons in the presence of cobalt catalysts. Nickel catalysts are known to effect the selective synthesis of methane,[15] although it has been recently reported[16] that the coprecipitated Ni–Ti–Mg catalysts, promoted with Na and Cu, are effective in the synthesis of higher aliphatic alcohols. A distinctive feature of the ruthenium catalyst is its capacity to effect the formation of high-molecular-weight polymethylenes from CO and H_2. Other Group VIII metals (Ir, Pd, Pt, Os, and Rh) exhibit an insignificant activity in the Fischer–Tropsch (FT) synthesis.

As a consequence of the increased interest in the FT synthesis after the petroleum embargo in 1973, there was a sharp increase in the number of publications on this question. Among them, mention must be made of certain monographs[14,17,18] and reviews.[15,19–31]

However, the latest complete review devoted directly to the mechanism of the FT synthesis in the Soviet periodical literature dates back to 1967,[32] although this topic has been briefly discussed in a number of communications by Soviet authors.[33–37]

II. The carbide mechanism

The first version of the carbide mechanism was proposed by Fischer and Tropsch. They suggested that this mechanism involves the formation of metal carbides and their hydrogenation to oxygen-free intermediates (for example, methylene species), whose polymerisation leads to the formation of the set of products observed.[2,3,88] In the course of the development of these views, a more detailed mechanism, supported by certain kinetic studies, was proposed.[39,40]

After this hypothesis had been forgotten for many years, there has been an appreciable growth of interest in it during the last 8–10 years. Furthermore, at the present time this is regarded as one of the main hypotheses.

The "neocarbide" theory originated from the studies by Wentercek et al.[41] and Araki and Ponec.[42] The elegant study by Goodman and Yates,[43] using doubly labelled CO, also confirmed the presence of a carbon monoxide dissociation stage in the FT synthesis. The formation of the following intermediate species on the (111) surface of nickel has been established by secondary ion mass spectrometry (SIMS):[44] C^+, CH^+, CH_2^+, CH_3^+, O^+, CD^+, CD_2^+, CD_3^+, $NiCO^+$, $NiOH^+$, $NiCH_2^+$, $NiCH_3^+$, $NiCH^+$, and NiC^+. It has been shown that surface oxygen-free species of the type CH_x (x = 0–3), formed via the CO dissociation stage, are intermediates on the Ni, Co, and Ru catalysts deposited on SiO_2.[45] In the study quoted, the Ni, Co, and Ru catalysts were first converted into the carbide form with the aid of ^{13}CO. The subsequent interaction of ^{13}CO and H_2 on their surface led to the formation of $^{13}CH_4$ methane and a number of normal alkanes containing several ^{13}C atoms in a single molecule, i.e. the carbide carbon participates in the formation of hydrocarbons.

The possibility of the rapid dissociative adsorption of CO on typical metallic catalysts of the FT synthesis and the presence of this stage, as the initial stage, in the mechanism of such synthesis have been confirmed by a series of experimental data and a large group of supporters.[46-53]

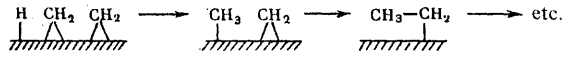
A significant confirmation of the carbide hypothesis was obtained in two investigations.[54,55] In the decomposition of diazomethane in the presence of hydrogen over a typical FT synthesis catalyst (Ru, Co, Fe), a mixture of mainly linear alkanes and alkenes was formed. The proportions of the products obeyed the Schulz–Flory equation and was typical for syntheses from CO and H_2. For practical purposes, it is convenient to express this equation in the logarithmic form

$$\lg(m_P/P) = \lg(\ln^2\alpha) + (\lg\alpha)P,$$

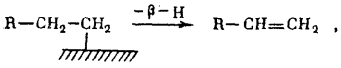
where P is the number of carbon atoms in the product molecule, m_p the weight fraction relative to the overall product, of the hydrocarbon (or the oxygen-containing compound) in which the number of carbon atoms is P, α is the probability of chain propagation defined as $\alpha = r_p/(r_p + \Sigma r_{tr})$, where r_p and r_{tr} are the rates of chain propagation and transfer respectively. If the molecular weight distribution obeys this equation, then the plot of $\lg(m_p/P)$ against P should be represented by a straight line. Furthermore, in this equation there is an "internal control", since α is determined both by the slope ($\lg\alpha$) and the intercept on the ordinate axis [$\lg(\ln^2\alpha)$]; the two values obtained should be identical.

C_1-C_{18} hydrocarbons have been obtained from $CH_2N_2 + H_2$ and $CO + H_2$ mixtures over Co and Fe, the selectivity of their formation depending in both cases to equal extents on the reaction conditions. Thus the increase in the H_2 partial pressure led to an increase in the alkane : alkene ratio and to a decrease of the average molecular weight. High molecular-weight polymethylenes were formed over Ru in both cases, which is typical of catalysts of this kind.[6] On the other hand, the decomposition of diazomethane in the presence of H_2 over Ni and Pd yielded not only methane but also higher hydrocarbons, although nickel is known to be a typical methane formation catalyst. However, at a pressure of 68 atm, the proportions of the products of the synthesis from CO and H_2 in the presence of this catalyst proved to be close to those obtained in experiments involving the treatment of the nickel catalyst with hydrogen for 1 atm after the decomposition of diazomethane over it. In the decomposition of the $CH_2N_2 + H_2$ mixture over Cu, only methane and ethylene were detected in the reaction products.

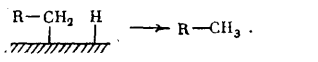
The gas-phase decomposition of diazomethane itself over metallic catalysts at 200 °C under the conditions used led in all cses to the formation of only one product–ethylene. Hence it follows that, in the absence of H_2, the methylene intermediates formed only dimerise with subsequent desorption of ethylene as the final product; the oligomerisation of the intermediate has not been observed. On the basis of the similarity of the proportions of the products of the conversion of $CO + H_2$ mixtures, on the one hand, and $H_2 + CH_2N_2$ mixtures, on the other, it has been concluded[54,55] that the mechanisms of the two processes are identical and that the methylene intermediates may polymerise, the polymerisation being initiated by the presence of the M–H bond on the catalyst surface. Although the authors[54,55] did not investigate the possible ways of the generation of CH_2 fragments on the catalyst surface, it had been noted earlier that the CH_x fragments on typical catalysts of the FT synthesis can be formed as a result of the hydrogenation of the carbides produced on the surface in the dissociative adsorption of CO. In their view, the data presented confirm the carbide hypothesis[23,38] and make it possible to justify the following mechanism proposed initially by Biloen et al.:[45]



Chain termination takes place either as a result of the elimination of β-hydrogen atoms with formation of α-olefins, i.e.



or as a consequence of the reduction of the M–C bond and the formation of alkanes:



We may note that in the studies quoted[54,55] only one feature of the carbide mechanism was demonstrated—the ability of the methylene intermediates to form hydrocarbons on polymerisation, but the question of the ways in which these intermediates arise under the conditions of the real synthesis from CO and H_2 in the absence of diazomethane remained unresolved.

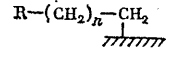
As regards the question of the origin of the CH_2 fragments on the catalyst surface, we may note that they may be formed both on the metal carbide (as a result of the interaction of hydrogen with the M–C intermediate arising in the dissociative adsorption of CO) and via the stepwise hydrogenation of the non-dissociatively chemisorbed CO. The answer to this question actually determines whether the carbide mechanism operates in a particular catalytic system.

Since the involvement of the CH_2 intermediates both in the chain initiation and chain propagation stages is postulated only in the carbide mechanism of the FT synthesis, the experimental data quoted by Brady and Pettit[54] concerning the influence of the additional $^{12}CH_2$ groups obtained by the preliminary decomposition of diazomethane on the proportions of the products in the synthesis from ^{13}CO and H_2 in the presence of a cobalt catalyst are consistent solely with the carbide hypothesis. Furthermore, in the experiment on the Co catalyst using mixtures of ^{13}CO, H_2, and $^{12}CH_2N_2$, the distribution of ^{13}C and ^{12}C in the propane formed also corresponds only to the carbide mechanism.

Analogous conclusions have also been reached in a study[56] where CH_xCl_{4-x} (x = 1–3) was used as the source of the surface CH_x intermediates.

However, the possibility of the formation of different forms of carbon in the dissociative adsorption of CO[57-60] very greatly complicates the question of the mechanism of the formation of methylene intermediates on the catalyst surfaces.

The carbide hypothesis presupposes that different alkyl fragments of the type

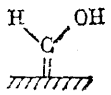


are present on the surface as intermediates in the chain propagation stage. Use of the novel method of the so called "chemical trapping agents" (pyridine, cyclohexene)[61-63] made it possible to demonstrate that alkyl intermediates are precursors of the hydrocarbons obtained.

Thus the set of experimental data available at present makes it possible to regard methylidyne, methylene, methyl, and R-alkyl species bound to the surface as possible intermediates in the FT synthesis. The carbide mechanism explains satisfactorily the formation of different hydrocarbons. On the other hand, the appearance of oxygen-containing products, which are known to be capable of predominating in the overall products under certain conditions, is inexplicable in terms of this mechanism. The explanation of the presence of oxygen-containing compounds in the reaction products by postulating a chain termination stage as a result of the insertion of CO in the M–C(Alk) bond in the carbide mechanism[25,64] is rather unconvincing, since this chain termination pathway does not explain the entire wide variety of the oxygen-containing reaction products formed.

III. The condensation mechanism

In the 1950's Stroch et al.[65] and independently Eidus[32] put forward the hypothesis that hydroxymethylene groups are formed on the surface of the metal from the adsorbed CO and the chemisorbed atomic hydrogen and that C–C bonds arise as a result of condensation with elimination of water. The following arguments have been quoted in support of this hypothesis: (1) the experimentally established fact that an adsorbed complex with the CH_2O stoichiometry is formed;[66–68] (2) the fact that the amount of CO and H_2 adsorbed from the mixture exceeds the overall amount of these substances adsorbed separately; (3) the detection of compounds having the composition CH_2O and other oxygen-containing intermediates[69] by gas-phase mass-spectrometry; (4) identification of oxygen-containing compounds on the surfaces of iron catalysts;[70] (5) evidence for the stability of chemisorbed complexes of the type[71]



based on quantum-chemical calculations.

However, it has been shown convincingly[37,72,73] that the possible contribution by processes involving the condensation of both methylene and hydroxycarbene intermediates is extremely insignificant, at least on iron catalysts. So far the condensation mechanism of chain propagation has not been widely recognised. Despite the major advances in organometallic chemistry, the occurrence of a condensation reaction of the type[22]

$$M{=}CHOH + M{=}CHOH \rightleftarrows M{=}CHCOH{=}M + H_2O$$

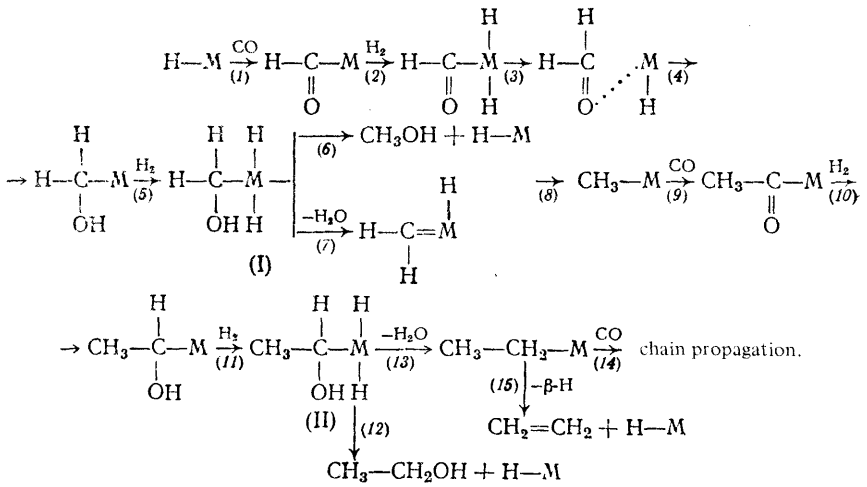
has not been established. However, the formation of oxygen-containing intermediates in the FT synthesis, which is at present the subject of vigorous discussion, has served as the basis of mechanisms which constitute an alternative to the condensation mechanism

IV. The mechanism based on the insertion of CO

The mechanisms of the FT synthesis according to which chain propagation is a result of the insertion of activated CO in the M–C bonds have been proposed by Schulz and co-workers[74,75] and later by Henrici-Olive and Olive.[76] Pichler and Schulz[74] postulate the formation of two-centre intermediate compounds, while Henrici-Olive and Olive[76] assume the possibility of a whole cycle of reactions on a mononuclear active centre. The mechanism proposed by Henrici-Olive and Olive (Scheme 1), most frequently discussed recently, is presented below:

In the first stage, CO is inserted into the M–H bond of the surface hydride and a primary formyl complex is formed. This is followed by stages involving the oxidative addition of H_2 [stage (2)] and the reductive elimination of the formyl ligand [stage (3)], leading to the formation of formaldehyde and a metal hydride. However, the formaldehyde does not leave the coordination sphere of the metal and remains bound to the active centre. The interaction of the metal hydride with the aldehyde [stage (4)] with subsequent oxidative addition of hydrogen [stage(5)] entails the

Scheme 1



appearance of the intermediate (I). The intermediate can be converted via two pathways: either as a result of reductive elimination [stage (6)], which leads to the formation of methanol and a metal hydride as the kinetic chain transferring agent, or as a result of the elimination of water [stage (7)] with formation of a carbene intermediate, which is converted into a σ-bonded methyl complex after rearrangement [stage (8)]. The next CO molecule is coordinated to the active centre and is inserted in the $M-CH_3$ bond [stage (9)], which leads to an acyl intermediate. Stage (10) corresponds to the sum of stages (2)–(4), but differs by the fact that the hydrocarbon chain becomes longer by one carbon atom. The oxidative addition of hydrogen [stage (11)] results in the formation of the intermediate (II), which is converted via reactions of type (6), (7), and (8) into either ethanol and a metal hydride [stage (12)] or into a metal alkyl [stage (13)]. The metal alkyl is either subjected to the insertion of the next CO molecule [stage (14)] and then propagates the growing chain or affords, after β-elimination of a hydrogen atom [chain termination—stage (15)], the final product—an α-olefin (ethylene in the given stage). According to the authors, the metal hydride is responsible for the occurrence of secondary hydrogenation and isomerisation reactions [reactions (16) and (17)]:

$$R-CH=CH_2 + H-M \begin{cases} \xrightarrow{(16)} R-\underset{\displaystyle M}{\underset{|}{CH}}-CH_3, \\ \xrightarrow{(17)} R-CH_2-CH_2-M. \end{cases}$$

Since α-olefins are the primary products of the synthesis, the predominance of methyl-substituted structures among the isomeric products becomes understandable.

The main evidence in support of this mechanism is its analogy with metal complex catalysis.[77–83] Thus the formation of alkylbenzenes in the presence of the $W(CO)_6.AlCl_3$ catalytic system has been considered as one of the decisive pieces of evidence:[78]

$$C_6H_6 + n\mathrm{CO} + H_2 \rightarrow C_6H_5(CH_2)_nH + H_2O, \quad n = 1-5,$$

the proportions of the alkylbenzenes obeying the Schulz–Flory relation. However, it has been shown that [84] the side chain in alkylbenzenes is formed with participation of the carbon atoms of the benzene ring: when carbon-labelled benzene was used, alkylbenzenes with the carbon label in the side chain were obtained.

Nevertheless, the migration insertion of CO in the $M-C$ bond is a well known reaction in the chemistry of carbonyl complexes.[85] In fact, this involves the migration of the alkyl group to the carbonyl ligand coordinated to the metal, which has been demonstrated for the reaction[86,87]

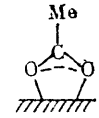
$$CH_3Mn(CO)_5 \underset{-CO}{\overset{+CO}{\rightleftarrows}} CH_3COMn(CO)_5.$$

There is also significant evidence that chain propagation in the FT synthesis takes place as a result of the insertion of CO in the $M-C$ bond.[88,89] The interaction of CO, H_2, and $C_6H_5C\equiv CH$ in the presence of a premelted iron catalyst yielded aromatic alcohols with C_3-C_8 side chains whose proportions obey the Schulz–Flory statistics. The introduction of phenylacetylene made it possible to synthesise aromatic alcohols at temperatures in the range 110–130 °C, but the reaction proper between CO and H_2 is not observed and the $C-C$ bonds can therefore be formed only as a result of the incorporation of CO in the chain without its preliminary interaction with H_2 and without dissociation (the mechanisms of the CO + H_2 + alkyne reactions will be considered below).

Attempts have been made[90,91] to detect on the surface of the working catalyst the structures postulated in the mechanism described. Convincing evidence for the existence of the acyl group



and the acetate



as precursors of the oxygen-containing C_2 compounds has been obtained by IR spectroscopy *in situ* on the surfaces of the Rh/SiO_2 and $Rh-Mn/SiO_2$ catalysts.[91] An attempt has also been made to detect structures of the acyl type on the Fe/SiO_2 surface using diethylamine as the chemical trapping agent. The reaction between the acyl carbon of the postulated oxygen-containing intermediate and diethylamine in the presence of hydrogen should have led to the formation of either *NN*-diethylamides or *N*-alkyldiethylamines. Among the reaction products, *NN*-diethylformamide, *NN*-diethylacetamide, and C_1-C_4 *N*-alkyldiethylamines were found in the experiment. However, this is not unambiguous evidence for the presence of oxygen-containing intermediates on the surface of the working catalyst, because the above products might have been formed via other pathways.

We may also note studies, [80–83] in which the latest experimental data confirming the carbide mechanism have been analysed.[80–83] It was shown that data[45,54,55] interpreted within the framework of the carbid theory do not nevertheless constitute unambiguous proof of the absence of the CO insertion stage as the chain propagation stage and that they are fully consistent with the mechanism proposed by Henrici-Olive and Olive.[76]

Kagan et al.,[37] who regard the synthesis of compounds from CO and H_2 as a heterogeneous-catalytic chain reaction initiated, as a result of the interaction of CO and H_2, by an oxygen-containing intermediate (chain initiation step), hold a similar view on the mechanism of the FT synthesis. Chain propagation takes place as a result of the successive addition of CO and H_2 to a hydroxymethylene complex of this kind or its homologues without a preliminary interaction between them. In the course of chain propagation, the complex undergoes intermediate dehydration and is lengthened by one CH_2 group with migration of the active centre to the end of the growing chain.

Aliphatic[92,93] and aromatic[89,94] alcohols, and α ω-diols or their monoethers[95] have been synthesised using respectively acetylene, phenylacetylene, and propargyl alcohol and its ethers as the third component.

Thus the possibility of a large series of syntheses based on CO and H_2 via the initiated hydrocondensation of CO was established. This method makes it possible to obtain compounds belonging to a wide variety of classes using the corresponding initiator (by varying the group R in the terminal alkyne $R-C\equiv CH$):

$$R-C\equiv CH + CO + H_2 \rightarrow R(CH_2)_nOH,$$
$$R = H;\ Ph,\ CH_2OH,\ CH_2OMe,\ CH_2OBu\text{-}t;\ n \geqslant 3.$$

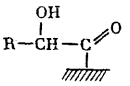
The presence of the $(CH_2)_nOH$ fragment is common to all these compounds.

Comparison of the syntheses of higher aliphatic alcohols from CO and H_2 [37] with the initiated syntheses showed that the mechanisms of these reactions are similar and probably differ solely by the chain initiation stage, i.e. by the way in which the primary complex is formed.

Detailed investigation of the mechanism of initiated syntheses by comparison with the available literature data suggested a mechanism of this process which accounts for the origin of the products detected (Scheme 2).†

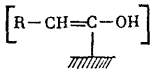
The studies published by Kline et al.[96] indicate the possibility of the formation of π-bonded acetylene $Fe_2(C_2H_2)$ when it interacts with the active centre of an iron catalyst. The idea that the chain initiation step involves the catalytic interaction of the alkyne with CO and H_2 is confirmed by the fact that the alkyne is in all cases incorporated only once in each molecule of the reaction product; its inclusion in the growing chain has not been observed.[88,97-99] This follows from the constancy of the molar radioactivity of C_3-C_9 alcohols in experiments with mixtures of CO, H_2, and $HC\equiv{}^{14}CH$.[97] Chain initiation takes place much more readily when alkynes are introduced into the mixture of CO and H_2. The syntheses with participation of these complexes can be achieved under conditions which are non-traditionally mild for the FT process: at temperatures in the range 110–130 °C and pressures in the range 25–50 atm. The products of the CO and H_2 interaction proper were not then detected. This agrees with the claim that the insertion of CO in the M–H bond is energetically more favourable than its insertion in the M–C bond.[100] The possibility of achieving initiated syntheses under mild conditions shows that the insertion of CO in the M–C bond is in fact the only possible way in which chain propagation can take place because the formation of intermediates as a result of the interaction of CO with H_2 or of reactions of CO itself would have naturally led to the appearance of the products of the interaction of CO and H_2.

The formation of the primary complex from CO, H_2, and the alkyne in the first stage of initiated hydrocondensation was confirmed by carrying out the homogeneous model synthesis of aromatic alcohols from CO, H_2, and iron carbonyl complexes of phenylacetylene. The set of products formed proved to be analogous to that obtained in the synthesis of aromatic alcohols from CO and H_2 with participation of phenylacetylene in the presence of a premelted iron catalyst.[99] In this case, chain propagation also proceeds via the insertion of CO in the Fe–C bond, as in the mechanisms considered previously in this Section.[74-76] This hypothesis is supported by the results of studies[101,102] in which the formation of hydroxyacyl complexes of the type



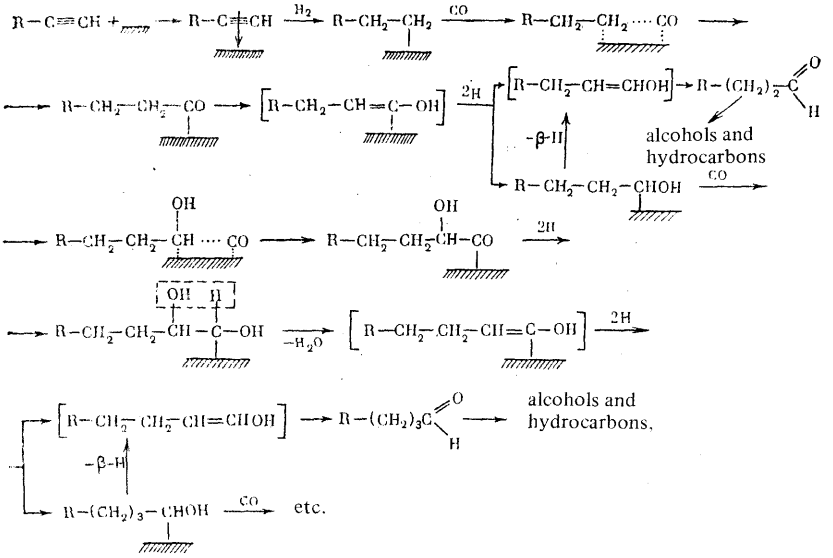
was established and the reaction involving the insertion of CO in the M–C bond in the hydroxyalkyl complex was achieved.

Surface enolic intermediates of the type



have been detected in the hydrogenation of ketones on the surface of premelted iron catalysts.[103]

Scheme 2



†See E V Slyvinsky, Yu P Voitsechovsky, and S M Loktev *Proceedings of the 9th International Congress on Catalysis, Calgary, 1988*, Vol. 2, p. 729

The possibility of the dehydration of diol structures with formation of surface enolic intermediates has been confirmed by carrying out the model reaction involving the dehydration of ethylene glycol to the expected acetaldehyde in the presence of the same catalyst.[104]

The detection of the R and CH_2OH groups in the reaction products in the α- and ω-positions respectively supports the hypothesis that, after the chain initiation step, the alkyne incorporated in the hydrocarbon chain moves away from the active centre without participating in the chain propagation stages. Comparison of the relative selectivities[105,106] shows that the primary products of the initiated syntheses are aldehydes, while alcohols and hydrocarbons are formed as a result of secondary hydrogenation reactions (probably via independent pathways).

Chain termination apparently occurs as a result of the β-elimination of hydrogen and its oxidative addition.

Although the majority of the reactions representing the individual stages of the mechanism based on the insertion of CO are known in organometallic chemistry, nevertheless for a long time it was not possible to achieve the homogeneous version of the FT synthesis. The advances in organometallic catalysts in recent years made it possible to obtain numerous pieces of evidence in support of these mechanisms (see Section VI).

V. Other mechanisms

The so called "hybrid mechanisms", in which the individual elements of different mechanisms are combined, have been considered recently in a number of studies. In their investigation of the influence of the Ni–Cu catalysts on the selectivity of the hydrogenation of CO, van Barneveld and Ponec[107] suggested that carbon monoxide is capable of dissociating on the surface, generating carbide carbon atoms, which are hydrogenated to hydrocarbon intermediates (for example, methylene species):

$$\left.\begin{array}{l} CO \rightarrow C + O \quad (a) \\ C + xH \rightarrow CH_x \quad (b) \end{array}\right\} \text{chain initiation.}$$

If a dual character of the adsorption of CO (with and without dissociation) is postulated, then chain propagation can proceed via the insertion of non-dissociatively adsorbed CO in the M–alkyl bond formed in the chain initiation stage with subsequent hydrogenation of the oxygen-containing intermediate:

$$\left.\begin{array}{l} CH_x + CO_{ads} \rightarrow (CH_xCO) \quad (c) \\ CH_xCO + nH \rightarrow H_2O + (CH_xCH_{n-2}) \quad (d) \\ CH_xCH_{n-2} + CO \rightarrow (C_2H_{(x+n-2)}CO) \quad (e) \end{array}\right\} \text{chain propagation.}$$

The oxidative addition of hydrogen to the intermediate surface complex leads to chain termination:

$$CH_xCH_{n-2} + yH \rightarrow \text{hydrocarbons} \} \text{ chain termination.}$$

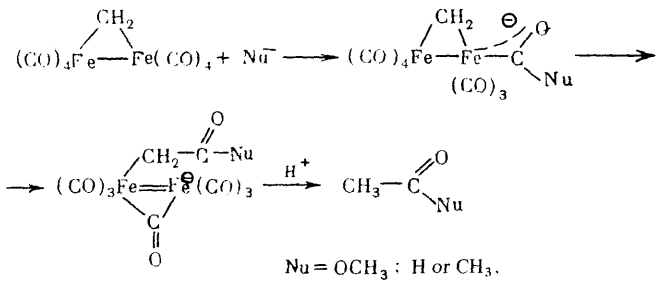
However, it had been shown earlier[108] that the only product obtained from carbide carbon on a premelted iron catalyst is methane.

A similar mechanism, combining the features of the carbide mechanism and the mechanism based on the insertion of CO, has also been adopted by Matsumoto and Benett.[109]

In a study of the Ru/SiO_2 and Co/kieselguhr systems, it was shown that only the conversion into methane takes place via the carbide mechanism, while C_n ($n \geqslant 2$) products are formed with participation of non-carbide intermediates.[110] A mechanism has been proposed for chain propagation, on the basis of the experimental data, via the condensation of hydroxylated intermediates:

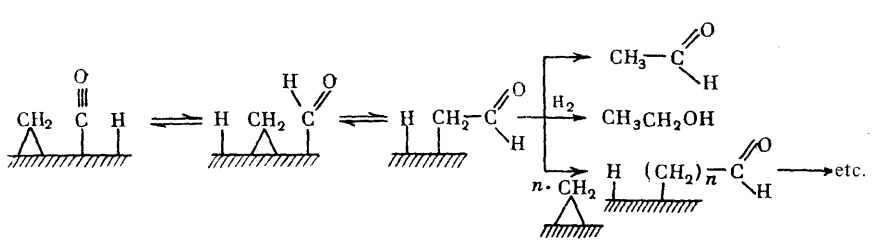
$$CH_4 \overset{2H_2}{\leftarrow} [C] + H_2O \rightleftarrows [CHOH],$$
$$2[CHOH] + H_2 \rightleftarrows [C_2H_4OH] + H_2O,$$
$$[C_2H_4OH] + [CHOH] + H_2 \rightleftarrows [C_3H_6OH] + H_2O.$$

The study of the characteristic features of the model stoichiometric reaction



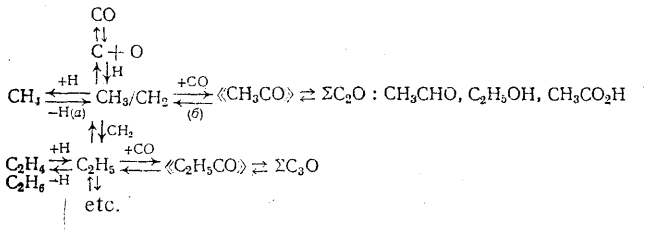
enabled Hackenbruch et al.[111] to postulate a novel hybrid mechanism, which has received definite confirmation in experiments on the synthesis from CO and H_2 in the presence of the Co/SiO_2 heterogeneous catalysis using methanol as the third component (nucleophile) and also in experiments with labelled reactants. The results agree with the postulated Scheme 3:

Scheme 3



Chain initiation takes place as a result of nucleophilic attack by the hydride on the CO molecule coordinated to the active centre with formation of a formyl intermediate. The interaction of the formyl group or its homologues (acyl groups) with the surface methylene intermediates leads to chain propagation, while chain termination is a consequence of the oxidative addition of hydrogen to M–C bond or the β-elimination of hydrogen.

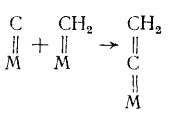
A mechanism has been proposed[113,114] for the formation of hydrocarbons and oxygen-containing products in the presence of promoted deposited rhodium catalysts on the basis of data obtained using ^{13}C-labelled reactants[112] and IR spectroscopy *in situ* under high pressure:[91]



The chain propagation in the formation reactions of hydrocarbons and oxygen-containing compounds includes the same stages and takes place on centres for the dissociative adsorption of CO, while chain termination probably occurs on different centres [stages (*a*) and (*b*)]. The C_n ($n \geqslant 2$) oxygen-containing compounds have a common precursor; for the C_2 compound, this is the "CH_3CO" acyl group formed when CO is inserted in a CH_3 or CH_2 surface hydrocarbon intermediate.

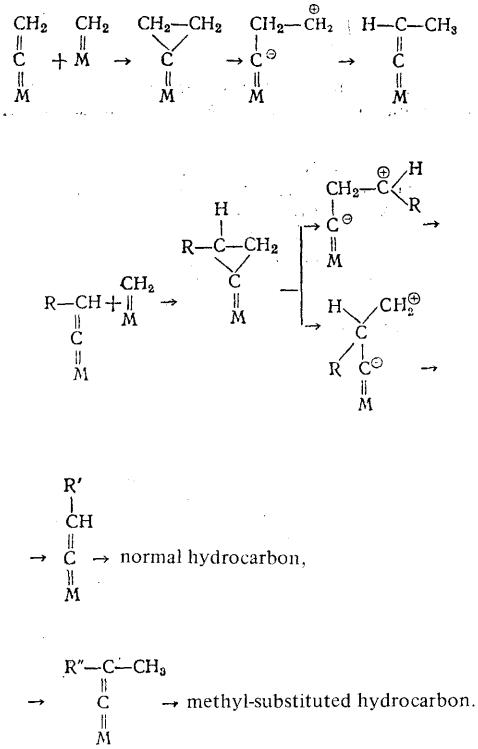
Analogous reaction mechanisms according to which oxygen-containing products and hydrocarbons are formed on different catalytic centres[90,115,116] or via different pathways,[117] had also been proposed previously. This was based on the difference between the coefficient α (the chain propagation parameter) in the Schulz–Flory equation for oxygen-containing products and hydrocarbons. However, according to data[118] for alcohols and hydrocarbons obtained in the presence of iron catalysts, the coefficients α are similar, which enabled Kagan et al.[37] and Berke et al.[119] to put forward the hypothesis that in the presence of iron catalysts, oxygen-containing compounds and hydrocarbons have a common precursor—a surface alkyl intermediate. The formation of methyl-substituted compounds as the principal isomeric products of the FT synthesis and the absence of a quaternary carbon atom in them was the reason why a modified version of the carbide mechanism was put forward.[120]

It is suggested that in this case the chain initiation stage involves the interaction of a surface carbon atom with a methylene intermediate to form the primary vinylidene complex:



Chain propagation takes place as a result of the interaction of the surface methylene groups with this complex to form a cyclopropylidene intermediate, which then readily rearranges to the normal or methyl-substituted homologues of the initial vinylidene complex:

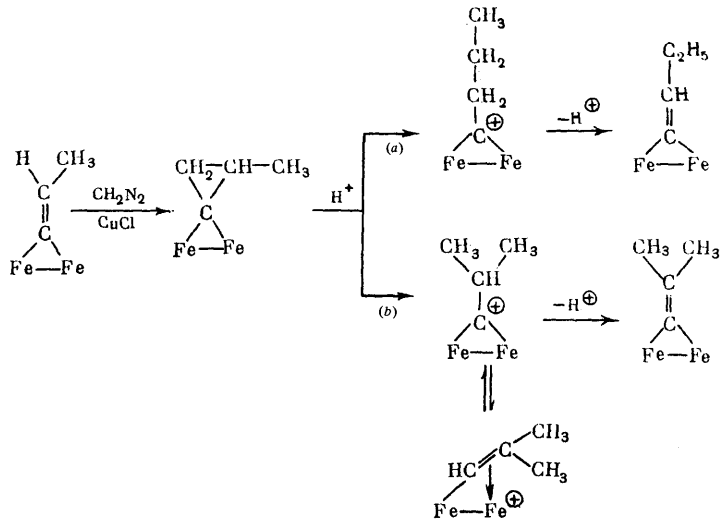
Scheme 4



Analysis of the stability of the carbonium ions formed made it possible to explain why the methyl-substituted products predominated and to put forward a mechanism for the formation of trace amounts of ethyl-substituted compounds.[120] In contrast to the insertion mechanisms described previously, here it is suggested that, in the growing vinylidene complex, the α-carbon atom in relation to the metal remains constantly bound to the metal and that the methylene intermediate is inserted in the double bond between the α- and β-carbon atoms in the surface compound.

However, the results of a study of the model homogeneous reaction of a cyclopropylidene complex of this kind permit the claim[121] that the methylene-vinylidene mechanism postulated[120] conflicts with experiment, because in the model reaction (Scheme 5) the pathway (*a*) does not occur (if the FT synthesis took place via the methylene-vinylidene mechanism, branched isomers should have predominated among its products, which has not been observed experimentally):

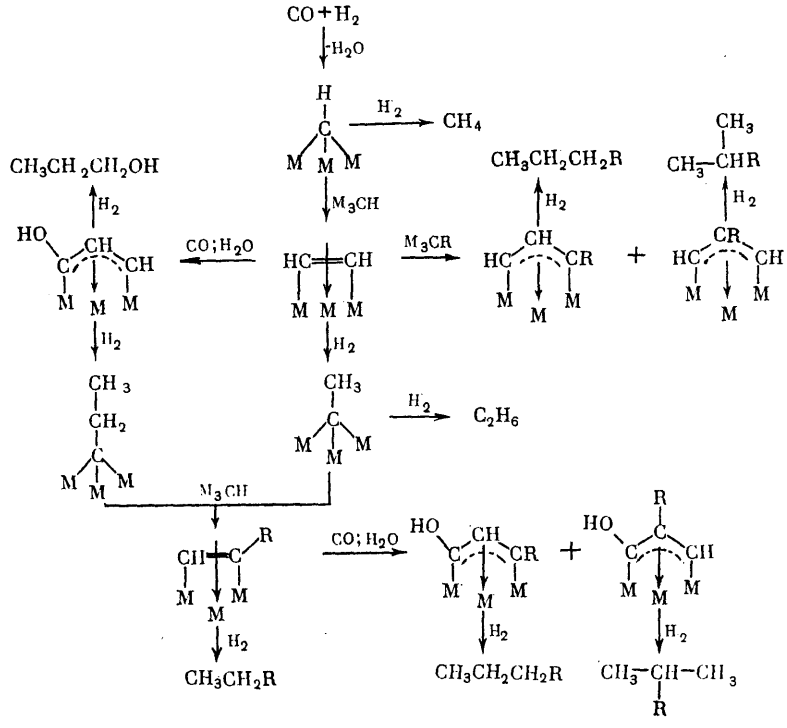
Scheme 5



On the basis of a model reaction carried out on ruthenium clusters, a mechanism has been proposed[122] for chain propagation, whose key stage is the addition of an alkyne to an alkylidyne (CR) with formation of a 1,3-dimetalloallyl, which is then hydrogenated and converted into an alkylidyne (CCH_2R) containing one CH_2 group more than the initial alkylidyne:

In the interaction of CO with H_2 on the surface, water and a surface methylene or methylidyne group are formed. The interaction of two methylidyne groups leads to the formation of an acetylene complex bound to the surface, whose reduction leads to the appearance of ethylidyne. The products of the hydrogenation of any alkylidyne is the corresponding alkane and the β-elimination of

Scheme 6



hydrogen from the intermediate containing more than two carbon atoms can lead to the formation of an α-alkene. The reaction of an alkyne with methylidyne or CO + H_2O leads to intermediates which serve as sources of the formation of branched hydrocarbons and oxygen-containing compounds. Analysis of the products of a model reaction carried out on a ruthenium cluster[122] permits the claim that the main products of the FT synthesis in this case should be unbranched compounds and that 2-methyl derivatives should predominate among the isomeric structures. According to Scheme 6, the principal oxygen-containing compounds are terminal functional compounds.

An interesting pathway leading to the formation of a C–C bond in the catalytic hydrogenation of CO has been proposed.[123] The authors[123] believe that the C–O bond is dissociated as a consequence of the deoxygenation of a formyl surface complex with its subsequent conversion into an alkyl surface compound. The only products of the deoxygenation of formaldehyde in its interaction with a titanium complex (I) were μ-oxotitanium complexes (II) and ethylene:

$$\underset{\text{(I)}}{2[CpTiCl_2(THF)_{1.5}]} + CH_2O \rightarrow \underset{\text{(II)}}{[CpTiCl_2]_2O} + CH_2{=}CH_2.$$

The data obtained suggested two mechanisms of the formation of ethylene (Scheme 7):

Thus one can postulate the possibility of the formation of surface CH_2 groups via the successive reactions

$$CO + H_2 \rightarrow (CH_2O) \xrightarrow{\text{deoxygenation}} (CH_2).$$

This pathway is an alternative to the mechanisms according to which the reaction of the CH_2O intermediate is accompanied by dehydration.[37,74,76]

An unusual example of the formation of a C–C bond has been described.[124] The carbonyl complex Tâ$(CO)_2(dmpe)_2Cl$ [dmpe = 1,2-bis(dimethylphosphino)ethane] was reduced to $Ta(Me_3SiOC{\equiv}COSiMe_3)(dmpe)_2(SeiMe_3)$, which contains an acetylenic diether ligand incorporating the C≡C multiple bond. A similar method of formation of a C–C bond in the reduction of the carbonyl ligand using metallic sodium had been described earlier.[125]

VI. The mechanism of the Fischer–Tropsch synthesis from the standpoint of organometallic synthesis

The vigorous investigation of reactions involving the homogeneous hydrogenation of carbon monoxide during the last few years[126] made it possible to obtain interesting information about the mechanisms of the individual stages of this reaction and about the structures and reactivities of the postulated intermediates in the FT synthesis.

In a number of studies,[28,127–135] it has been postulated that CO is hydrogenated via the pathway

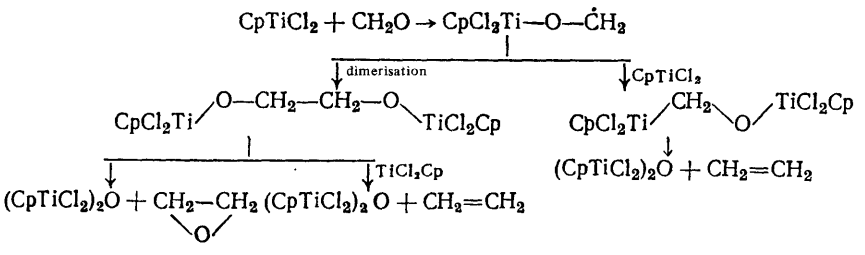
$$M{-}CO \rightarrow M{-}CHO \rightarrow M{-}CH_2OH \rightarrow M{-}CH_3,$$

in which the key intermediates are formyl and hydroxymethylene complexes.

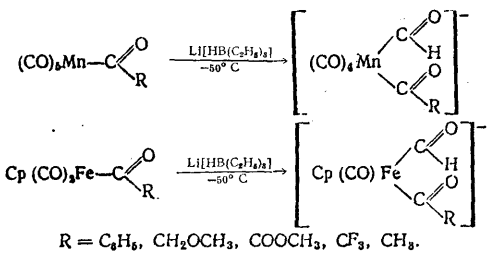
The first formylmetal complex has been obtained in a reaction with participation of the mixed anhydride of formic and acetic acids.[136] Subsequently the possibility of the hydride attack on the carbonyl coordinated in the metal complex was demonstrated convincingly in a series of model systems. Initially a large set of anionic formylmetal complexes was obtained by treating various metal carbonyls with strong hydride donors such as the trialkoxyboron hydrides $Na^+HB(OCH_3)_3^-$ and $K^+HB[C_3H_7\text{-iso}]_3^-$.[137] The structures of the mononuclear formylmetal complex $(C_2H_5)_2\overset{+}{N}.[3,5\text{-}(CH_3)_2C_6H_3O)_3P](CO)_3FeCHO^-$ and the dinuclear complex $(C_2H_5)_4\overset{+}{N}(CO)_9Re_2CHO^-$ have been most fully characterised.[138,139]

The formation of a series of unstable formylmetal complexes of many metals has been demonstrated with the aid of physicochemical analytical methods (IR spectroscopy, ^{13}C NMR, and especially ^1H NMR, because the proton in the $-C\overset{O}{\diagdown\!\!\diagup H}$ group gives rise to the characteristic chemical shift δ = 14–16 p.p.m.).[140] It is of interest that, on treating the anionic ion complex $(CO)_4FeCHO^-$ with hydrogen chloride, the formation of formaldehyde was observed. Treatment of osmium and iridium carbonyl clusters with hydride donors of the type of $Li[HB(C_2H_5)_3]$ leads to the reduction of one of the carbonyl ligands to the formyl ligand and the formation of the cluster anions $[Os_3(CO)_{11}CHO^-]$ and $[Ir_4(CO)_{11}CHO^-]$.[141,142] Carbonyl complexes containing acyl ligand as well as the formyl

Scheme 7



ligand synthesised:[143]

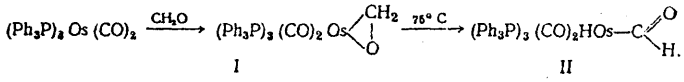


$R = C_6H_5,\ CH_2OCH_3,\ COOCH_3,\ CF_3,\ CH_3.$

The study of the properties of the fairly stable anionic iron carbonyl complex $[(C_6H_5O)_3P](CO)_3Fe-CHO$ showed that the formyl complexes can function also as hydride donors in relation to ketones, alkyl halides, and metal carbonyls (in the last case a new formylmetal complex is formed) and as "the target" of further hydride attack.[137,138]

Quantum-chemical calculations[144] indicate the instability of the formyl complex $[(CO)_4FeCHO]^-$, but analogous calculated data of the same workers[145] show that the alkali metal ion (Li^+), coordinated to the carbonyl ligand of the $[HFe(CO)_4]^-$ anion, promotes the insertion of CO in the Fe–H bond (the migration of the hydride group to the carbonyl ligand), affording a stable formyl complex in which the alkali metal ion is coordinated to the formyl oxygen.

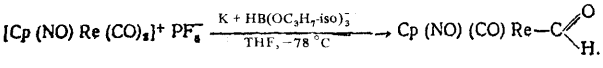
The neutral formylmetal complex (II) and not the anionic complex is probably a closer analogue of the surface intermediates formed in the FT synthesis. It was first detected when formaldehyde was added to an osmium carbonyl complex with subsequent rearrangement:[146]



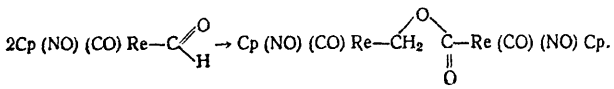
I II

The complex (I) contains coordinated formaldehyde, which can be regarded as a tautomer of the hydroxymethylene ligand $-C\begin{matrix}H\\OH\end{matrix}$.

The reduction of the carbonyl ligand to the formyl ligand via external transfer of hydride hydrogen was first achieved by means of the reaction [147]

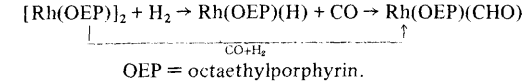


The complex Cp(NO)(CO)ReCHO has also been synthesised, isolated, and identified in other studies.[148,149] It has been shown that the formyl complex can behave as a hydride donor in relation to the formyl group:[150]



According to numerous data obtained in the study of the reactions leading to the formyl complexes of rhenium,[147–149] titanium,[151] and niobium and iron,[152] an obligatory condition for the formation of such compounds is probably only the outer-sphere transfer of hydride hydrogen as a result of the nucleophilic attack by strong hydride on the coordinated carbonyl.

However, there have been a number of reports[153–156] about the inner-sphere hydride transfer in carbonyl hydride complexes. Thus the complex $[CpFe(CO)_2H]$ in solution in an alcohol R–OH forms the intermediate $[CpFe(CO)(CHO)(ROH)]$, in which the formate HCOOR is produced as a result of the interaction between the ligands CHO and R–OH.[153] The synthesis of a formyl complex by the direct insertion of CO in the M–H bond has also been reported:[157–158] the authors of these studies achieved the following reactions:

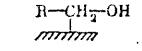


OEP = octaethylporphyrin.

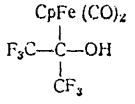
The formyl complex proved to be stable in the solid state and in solution in benzene.

Thus the possibility of the existence of the structures $M-C\begin{matrix}O\\H\end{matrix}$ as intermediates in the FT synthesis has been established for a large group of metals.

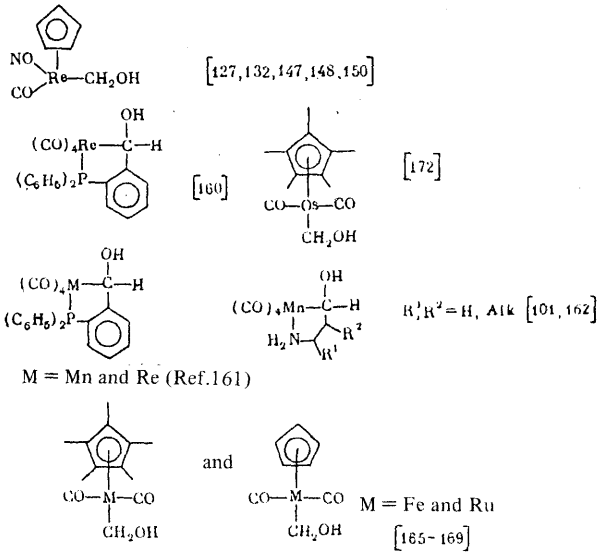
It was noted above that the involvement of the α-hydroxymethylene complex



as the most important intermediate has also been postulated in the mechanisms of the FT synthesis based on the insertion of CO. A structure close to the hydroxymethylene structure was first identified by Blackmore et al.:[159]



Subsequently it was possible to obtain similar complexes for rhenium,[101,127,132,147,148,150,160–162] osmium,[163,164] iron,[119,165–169] ruthenium,[165–169] manganese,[101,161,162] and rhodium.[170,171] Some of them are presented below [the numerals in square brackets denote references (Translator)]:



M = Mn and Re (Ref.161)

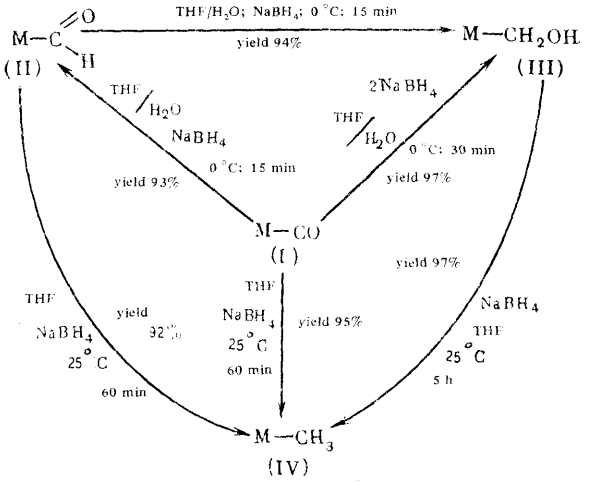
and

All the intermediate forms in the CO hydrogenation reaction in the presence of model systems have been isolated and identified.[148–150] The reduction of CO in the mononuclear rhenium

carbonyl complex has been achieved using $NaBH_4$ as the reductant.[148] The existence of the postulated stages and intermediates in the FT synthesis, namely M–CO, M–CHO, $M-CH_2OH$, and $M-CH_3$, has been demonstrated.

The authors were able to obtain, isolate, and identify the following compounds: $CpRe(CO)(NO)CHO$ (II), $CpRe(CO)(NO)CH_2OH$ (III), and $CpRe(CO)(NO)CH_3$ (IV). It was established that the reduction reaction pathways are in accordance with the parallel-consecutive Scheme 8:

Scheme 8

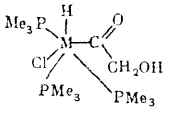


Similar results have been obtained in other studies.[149,150]

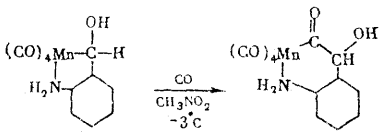
Although the possibility of the migration insertion of CO in the M–C bond has been demonstrated,[85-87] the attempts to achieve the formation of an α-hydroxyacyl complex in the presence of the hydroxylated complexes indicated via the reaction

$$M-CH_2OH \xrightarrow{CO} M-\overset{\overset{O}{\|}}{C}-CH_2OH$$

were unsuccessful.[132] Such a hydroxyacyl complex is assumed to be an intermediate in certain mechanisms of the FT synthesis. A complex of this kind has, however, been obtained recently by the oxidative addition of 2,5-dihydroxy-1,4-dioxan to $(C_8H_{14})M(PMe_3)_3Cl$, where M = Ir or Rh:[102]

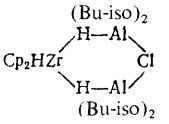


A hydroxyacyl complex is also formed in the carbonylation of an α-hydroxyalkyl complex:[101]

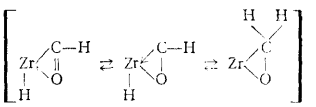


The possibility of the formation of diacyl complexes of the type $PhCH_2-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-M(CO)_4$ as a result of the double insertion of CO has been demonstrated.[173,174]

Cases are known where the hydrogenation of carbonyl ligands leads to the formation of not only the oxygen-containing products, typical for catalytic reactions based on CO and H_2. Thus it has been shown[175] that the following complex is formed in a solution of diisobutylaluminium hydride (DIBAH) in the presence of Cp_2ZrCl_2:

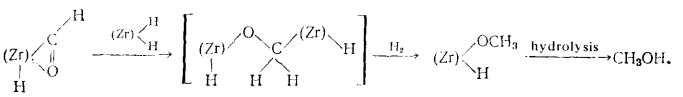


Its treatment with carbon monoxide at a pressure of 1–4 atm and room temperature leads to the precipitation of $CpZrCl_2$ and the formation of a mixture of aluminium alkyls, the hydrolysis of the latter resulting in the formation of aliphatic C_1-C_5 n-alcohols. The proposed reaction mechanism includes the dissociation of the complex with elimination of DIBAH and the liberation of a coordination site at the Zr atom. Intramolecular migration of the Zr–H hydride or external attack on the Al–H hydride is tentatively the first stage in the reduction of CO. There are data indicating the stoichiometric reduction of CO to methanol using pentadienylzirconium complexes.[127,153] On the basis of a series of indirect data, it has been postulated that a formylzirconium hydride complex is a key intermediate:



Such binding of the formyl ligand ensures, according to the authors, its stabilisation. The methoxy-ligand is formed in accordance with Scheme 9:

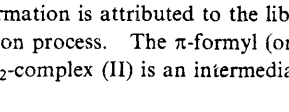
Scheme 9



A similar scheme has been described by Fachinetti et al.[176]

C_1-C_4 hydrocarbons have been obtained by treating $(CO)_5MnCH_3$ or $CpFe(CO)_2CH_3$ with carbon monoxide and B_2H_6.[177]

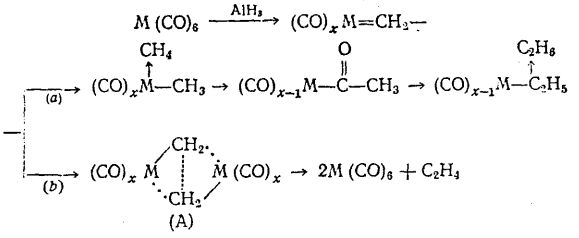
The homogeneous hydrogenation of CO to methane has been achieved[129] using $Cp_2Ti(CO)_2$. After the reaction, the active titanium complex is converted into the inactive octanuclear cluster $Cp_6Ti_8O_8$, whose formation is attributed to the liberation of water in the methane formation process. The π-formyl (or η^2-formyl) complex (I) or the μ_2-complex (II) is an intermediate in this case:



The stoichiometric reduction of CO in the interaction of $CpNbH_3$ with the metal carbonyls $M(CO)_6$, where M = Mo, W, or Cr, at 45 °C and a pressure of 1 atm in the presence of hydrogen leads to the formation of a mixture of C_1-C_3 hydrocarbons (the main product is C_2H_6).[178]

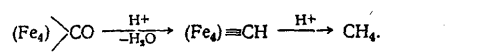
The stoichiometric model reaction involving the multistage reduction of CO to valeric acid has been achieved recently. After treatment with strong hydrogenating agents ($LiAlH_4$ or $NaBH_4$), the complex $[CpFe(CO)_2(PMe_3)]^+PF_6^-$ was converted into $Cp(PMe_3)(CO)FeMe$. Treatment of this complex with carbon monoxide at atmospheric pressure in the presence of $AgBF_4$ in tetrahydrofuran (THF) or CH_2Cl_2 led to the acyl complex $Cp(PMe_3)(CO)FeC(O)Me$, the reduction of which with tetrahydroborates afforded the alkyl complex $Cp(PMe_3)(CO)FeEt$. Numerous repetition of the CO insertion reaction and of the reduction of the resulting acyls made it possible to obtain the compound $Cp(PMe_3)$. .$(CO)FeC(O)Bu$. Finally treatment of this acyl complex with bromine water led to valeric acid $CH_3(CH_2)_3COOH$.[179]

The conversion of CO and H_2 into ethylene with a selectivity of 95% (the remainder being ethane and traces of methane and propane) in the $M(CO)_6$ (M = Cr, Mo, or W) system in the presence of a fourfold excess of AlH_3 in THF at 22 °C has been reported.[180] Experiments with deuterium have shown that AlH_3 is the only source of hydrogen. In order to account for the "anomalous" selectivity with respect to ethylene, the authors suggested the existence of carbene intermediates (A):

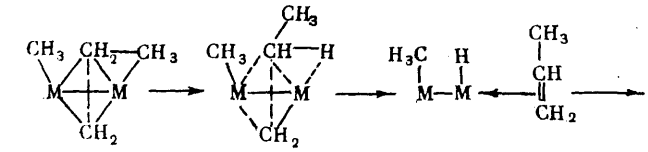


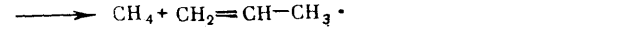
The pathway (*a*) includes the CO insertion stage leading to the formation of C_2 and C_3 hydrocarbons, while the pathway (*b*) leads to the dimerisation of the carbene intermediates, which gives rise to ethylene. The pathway (*b*) is probably preferred. Similar conclusions have been reached in other investigations.[181,182]

An interesting method of reducing CO by protonating polynuclear clusters with strong acids has been applied.[183] Treatment of the anionic cluster $[Fe_4(CO)_{13}]^{2-}$ with the strong protonating agent HSO_3CF_3 at room temperature led to the formation of methane, its yield depending greatly on the acidity of the medium. Isotope data showed that methane is formed from the carbonyl ligand as a result of the direct attack by an acid proton; after the elimination of water, a carbide is formed whose hydrogenation leads to methane:

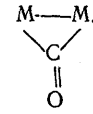


Interesting data supporting the carbide mechanism of the FT synthesis have been obtained in a study of the interaction of $[(RhC_5Me_5)_2Cl_4]$ with $LiCH_3$, which resulted in the formation of *cis*- and *trans*-$[(RhC_5Me_5)_2(\mu\text{-}CH_2)_2Me_2]$.[184] Propene, methane, and traces of ethylene are formed on pyrolysis of the *trans*-isomer, which confirms the possibility of the polymerisation of methylene species on the metal surface, initiated by a metal hydride, as the key stage in the carbide mechanism:

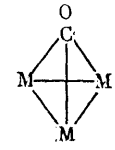




Much work has been devoted in recent years to the creation of homogeneous catalysts of the FT synthesis. It was shown in 1977[185] that the carbonyl clusters $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$ in toluene at 140 °C, a synthesis mass ratio ($CO:H_2 = 1:4$), and a pressure of 2 atm convert the CO + H_2 mixture into methane at an insignificant rate (the degree of conversion of CO is 1% after 3–5 days). The addition of PPh_3 or PMe_3 increases slightly the activity of the catalysts and leads to the appearance of traces of ethane and propane. The authors note that the reduction of CO requires specifically polynuclear clusters in order to achieve the many-centre CO–metal interaction. Such activation of CO reduces greatly the C–O bond order.[19,186] It has been suggested[19,187] that cluster systems make it possible to model more effectively the characteristics of heterogeneous catalysis than mononuclear homogeneous systems. When CO is coordinated to two or more transition metal atoms, the bond order is greatly reduced. Thus whereas terminal carbonyl ligands are usually characterised by $\nu(CO) = 2000-2100\ cm^{-1}$, for bridged carbonyl complexes $\nu(CO) = 1700-1850\ cm^{-1}$ is characteristic of CO ligands bound to two metal atoms:



The bridged carbonyls linked to three metal atoms,



are characterised by an even greater decrease in the bond order involved in the binding of CO, because $\nu(CO) \simeq 1600\ cm^{-1}$ for μ^3-CO.[21]

The significant role of Lewis acids as effective cocatalysts in the homogeneous CO hydrogenation reaction has been confirmed in a study[188] that was a continuation of investigations initiated by Thomas et al.[185] Thus the clusters $Ir_4(CO)_{12}$, $Rh_6(CO)_{16}$, $Rh_4(CO)_{12}$, and $Ru_3(CO)_{12}$ exhibited a high activity in the homogeneous CO-hydrogenation reaction in $AlCl_3$, $AlBr_3$, or BBr_3 melts at 180 °C and 1 atm, the activity of, for example, $Ir_4(CO)_{12}$, being approximately 100 times greater under these conditions than in the absence of the Lewis acid.[188] The reaction products were C_1-C_4 hydrocarbons and their ratios depended greatly on the reaction conditions—temperature, pressure, and the catalytic system used.

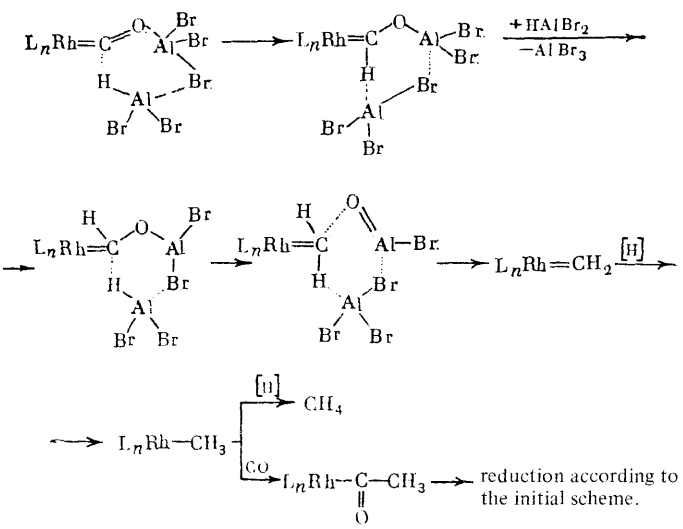
The carbonyl cluster $Os_3(CO)_{12}$ (the precursor of the catalyst) and BBr_3 (solvent and cocatalyst) proved to be active in the hydrogenation of CO to C_1-C_5 hydrocarbons.[189] It was shown that the osmium cluster $Os_2(CO)_6Br_4$, acting as the catalyst, is formed during the reaction.

Comparison of the data of Demitras and Muetterties[188] and Choi and Muetterties[189] with those of Thomas et al.[185] permits the conclusion that the presence of the Lewis acid does indeed stimulate the formation of the C–C bond in the hyrogenation of CO. It has been suggested[189] that BBr_3 facilitates the insertion of CO in the Os–C bond with formation of intermediates of the type $Os-CR-OBBr_3$.

Similar results have been obtained in the presence of the complex $Ir_4(CO)_{12}$ in a flow reactor, where the productivity of 0.2 mol of CO per mole of $Ir_4(CO)_{12}$ per minute was achieved with respect to C_1-C_6 hydrocarbons.[190]

When the $M_n(CO)_m-AlBr_3-Al$ homogeneous catalytic system was used, a mixture of C_1-C_4 hydrocarbons was formed from CO and H_2.[191,192] The metals tested fell within the following series in terms of their activities: Rh > Ir > Ru > Os > Ni. Under the catalytic conditions, an aprotic system possessing strong reducing and acid properties is formed in this case. The binding of the water evolved in the reduction process prevents the decomposition of the catalytic process. Apart from aluminium, magnesium or $LiAlH_4$ may be used as the reductant. The following mechanism has been proposed on the basis of the experimental data:[192]

Scheme 10

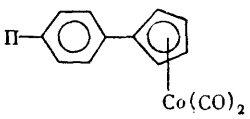


A whole series of processes involving the reduction of CO by hydrogen in the presence of soluble Rh clusters at high temperatures and very high pressures have been patented.[193] The reaction products are methanol, ethylene glycol, and propylene glycol. The true catalyst is the polynuclear anionic cluster $[Rh_{12}(CO)_{34}]^{2-}$ formed under the reaction conditions from various precursors.

It has been suggested that the rhodium bis-sulphide cluster $[Rh_{17}(CO)_{32}(S)_2]^{8-}$ be used for the conversion of the CO + H_2 mixture into aliphatic alcohols.[194]

As already mentioned above, it is best to use polynuclear metallic active centres in the hydrogenation of CO. However, some workers believe that the active centre for the hydrogenation of CO has the structure of a mononuclear complex.[133] The homogeneous hydrogenation of CO by hydrogen to ethanol (main product), ethanol, propanol, and the formates of these three alcohols using as the catalyst the mononuclear carbonyl hydride $HCo(CO)_4$, formed under the reaction conditions from the $Co_2(CO)_8$ cluster, has been reported.[195] The conversion of the CO + H_2 mixture into methanol and methyl formate has been observed using the ruthenium clusters, unstable under reaction conditions (225–275 °C, 1300 atm) as the catalyst precursors.[196] It was then established that the true reaction catalyst is mononuclear ruthenium pentacarbonyl $Ru(CO)_5$.

Mention should be made of a study[197] in which the homogeneous hydrogenation of CO to a mixture of C_1-C_{20} normal alkanes (170–200 °C, 30 atm, CO : H_2 = 1 : 3, solvent—n-octane) was achieved in the presence of an immobilised cobalt catalyst:



grafted to a polymer П. Control experiments established that activity in this reaction is shown in fact by the immobilised mononuclear cobalt centre and not by soluble cobalt compounds or metallic cobalt.

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In conclusion one should note that the enormous amount of experimental data concerning the mechanism of the FT synthesis accumulated at the present time makes it possible to assume confidently that the reaction proceeds via a multiplicity of pathways. The preference for a particular pathway is determined by the composition of the catalyst, the conditions of the synthesis, and a number of factors, the type of catalyst being decisive.

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