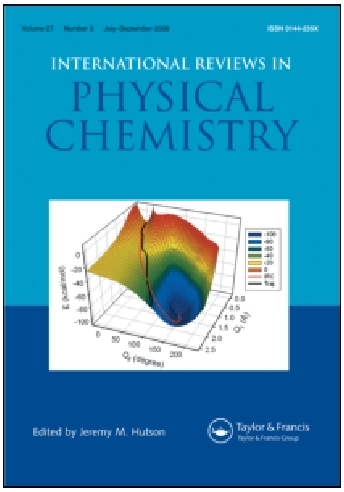

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Development of Ideas on the Mechanism of Low-Pressure Synthesis of Hydrocarbons From CO and H_2

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DEVELOPMENT OF IDEAS ON THE MECHANISM OF LOW-PRESSURE SYNTHESIS OF HYDROCARBONS FROM CO AND H_2

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ABSTRACT

The mechanism of Fischer–Tropsch synthesis of hydrocarbons by catalytic hydrogenation of carbon monoxide has not as yet been definitively resolved, even though considerable advances have been made. This article outlines the origin and development of the main ideas on the initiation, build-up and termination of the synthesized hydrocarbon chains. The original theory of the synthesis, involving carbidic surface intermediate, and objections against it are discussed. An account is given of its temporary rejection in the 1950s in favour of the theory of oxygenated surface intermediates. The arguments leading to the rehabilitation of the carbide theory in the mid-1970s and the current mechanistic views are presented.

1. INTRODUCTION

During the 1970s, the need for alternative sources of fuels and petrochemical feedstocks which could replace oil and natural gas led to a revival of interest in the synthesis of hydrocarbons and their oxygenated variants from carbon monoxide and hydrogen (synthesis gas, syngas) produced from coal.

The production of valuable by-products from the reaction of CO and H_2 can be traced back to Sabatier and Senderens. In 1902, they reported that methane was formed when a mixture of CO, CO_2 and H_2 was passed over dispersed nickel or cobalt at atmospheric pressure and 200–300°C (Pichler, 1952). But systematic research was started only by German scientists in the early 1910s. It led to patent applications claiming catalytic hydrogenation of CO at 100 to 200 atmospheres and 300 to 400°C to mixtures of alcohols, aldehydes, ketones, fatty acids and hydrocarbons (Pichler, 1952). Conditions narrowing the range of products and controlling their ratio were specified in further work. Thereby industrial production of methanol on this base was made possible, and was started in Germany and the USA in 1923 and 1927, respectively (Frohning, 1980). Higher homologues of methanol, and ethylene glycol can also be made the principal products of the process (Falbe, 1977; Frohning, 1980).

Disregarding some early non-systematic attempts by which mainly methane was obtained, Fischer and Tropsch of the Kaiser Wilhelm Institute for Coal Research in Mülheim/Ruhr are rightly considered as the true parents of hydrocarbon synthesis from CO and H_2. In their experiments on the preparation of the so-called Synthol, a

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mixture of oxygenated compounds and hydrocarbons, they observed that increasing amounts of alkanes were produced as the pressure and temperature were decreased (Pichler, 1952). Systematic research led to the practical elimination of oxygenated products, and thus in 1925 the low-pressure Fischer–Tropsch synthesis of hydrocarbons from CO and H_2 on iron- and cobalt-based catalysts at 1 to 7 atm and 250–300°C was born (Fischer and Tropsch, 1926a). In 1936, Fischer and Pichler announced the feasibility of the synthesis at medium pressures of 5 to 30 atm (Pichler, 1952, 1973).

Following technical development of the low- and medium-pressure processes, nine plants were put into operation in Germany between 1935 and 1939 for the synthesis of hydrocarbons on cobalt-based catalysts with a capacity of about 700 000 tons per year (Kölbel, 1957; Falbe, 1977; Frohning, 1980). This accounted for approximately 20% of the synthetic fuel produced in Germany (with direct hydrogenation of coal accounting for the remainder). Hydrocarbons from the Fischer–Tropsch process initially served mainly as motor fuels, but in 1944 40% of the production was used as feedstock for the German chemical industry (Kölbel, 1957). The originally applied cobalt-based catalysts were gradually replaced by iron-based catalysts (Pichler, 1952).

In the meantime, ruthenium was discovered to catalyse at pressures of 1000 to 2000 atm formation of polymethylene, a mixture of alkanes of molecular weight exceeding 20 000 and melting point above 130°C (Pichler, 1952; Falbe, 1977). Another new achievement was the high-pressure synthesis of branched hydrocarbons ('iso-synthesis') in the presence of oxide catalysts (Pichler, 1952; Cohn, 1956). Kölbel and co-workers proposed a modified technology: CO is fed together with water vapour to a catalyst suspended in a liquid medium, where a part of the CO is oxidized by water to CO_2 (water–gas shift reaction), while the hydrogen produced reacts with CO (Kölbel, 1957; Falbe, 1977; Kölbel and Ralek, 1980). All the processes producing hydrocarbons from CO and H_2 on metal catalysts are generally called Fischer–Tropsch (F–T) reactions, although the two authors jointly advanced only the low-pressure version of the synthesis.

After World War II the energy and chemical industries began to be directed towards oil. F–T synthesis was losing its economic attractiveness (Kölbel, 1957), and the last plant in Germany was closed in 1962. An exception to this trend has been represented by the Republic of South Africa. The first plant of its complex SASOL (South African Synthetic Oil Ltd), which was put into operation in 1955, reached a capacity of 240 000 tons per year. In 1975, construction of SASOL II installation was started with the planned capacity of 1 500 000 tons per year. Building on SASOL III commenced in 1979 (Dry, 1981).

The 1973 oil embargo and the growing awareness of the limits to world resources of oil and natural gas prompted a number of industrial nations to make an effort to find alternative sources of energy and chemical feedstock. The possibility of utilizing coal for this purpose has received much attention; this has stimulated new research and development activity, especially in the field of F–T technology. The traditional problem of F–T synthesis has been its limited selectivity. Current studies show that the F–T catalysts can be made more selective by

1. Chemical modifications.
2. Deposition in pores of zeolites or aluminas.
3. Combining with a suitable zeolitic catalyst, giving a bifunctional or polyfunctional catalyst (King *et al.*, 1981).

Recent improvements of catalysts, reactor design and process regime have increased the selectivity of F–T synthesis considerably, indicating that F–T processing can be tailored to specific needs, can be made much more flexible than in former years, and can thus become generally viable from the commercial viewpoint (Haggin, 1981). The advantages and drawbacks of various competitive technologies and their comparison with F–T synthesis are currently under discussion.

Parallel with the technological perfection of F–T synthesis and methanation, the mechanisms of interaction of $CO + H_2$ have been intensively studied. Views on these mechanisms have been profoundly changing and developing. The present article attempts to review the important advances in the field from the early beginnings to the present.

2. THE FUNDAMENTALS OF THE MECHANISMS OF METHANATION AND FISCHER–TROPSCH SYNTHESIS

The thermodynamic analysis of the hydrogenation of carbon monoxide shows that both saturated and unsaturated hydrocarbons, as well as oxygenates (alcohols, ethers, aldehydes, ketones, acids) can be formed (Storch *et al.*, 1951; Anderson, 1956; Greyson, 1956). Which of these potential products predominate depends on the catalyst, temperature, ratio and total pressure of the reactants, and other conditions (Pichler, 1952; Schulz, 1977; Denny and Whan, 1978).

The present survey is confined to hydrocarbons. Thermodynamically the most stable hydrocarbon is methane, and this would be the dominant product if the synthesis were to approach equilibrium. Methane actually can be obtained with a high selectivity, while the other hydrocarbons are synthesized in more or less complex mixtures. However, modification of the electronic and/or geometric structure of the catalyst (promotion or inhibition by additives; effect of carbon, oxygen, and other products of the reaction; effect of the support and of the dispersion and concentration of metal crystallites; alloying; application of bi- and poly-functional catalysts, etc.), as well as technological factors can profoundly affect the selectivity of the synthesis as to

1. The length of the hydrocarbon chain.
2. The degree of hydrogenation (the proportion of saturated and unsaturated hydrocarbon produced).
3. The degree of isomerization (the occurrence of branched products).

A number of mechanistic schemes have been suggested for the formation of hydrocarbons from CO and H_2. Generally, three successive steps can be distinguished in this reaction:

1. Initiation, consisting in the formation of the primary reaction intermediate.
2. Propagation, in which build-up of the hydrocarbon chain takes place.
3. Termination, when the chain growth is stopped and formation of the hydrocarbon product is completed.

In addition, readsorption of the products can occur, giving rise to their isomerization, hydrogenation, or hydrocracking (Pichler *et al.*, 1964, 1967; Pichler and Schulz, 1970). These secondary processes can significantly modify the range of the reaction products.

The particular mechanisms and their development will be discussed in the following sections.

3. HYPOTHESIS OF THE CARBIDE INTERMEDIATE

(*a*) *Early views on the mechanism of methanation. The mechanism of hydrocarbon synthesis by Fischer and his school*

The early studies of the low-pressure hydrogenation of carbon monoxide to hydrocarbons were confined to methanation, i.e., to the cases in which no chain propagation occurred. In 1902 the findings of Sabatier and Senderens suggested, and the later experiments of Fischer and his co-workers confirmed, that neither activation of hydrogen nor activation of carbon monoxide represented the steps governing the CO hydrogenation (Fischer *et al.*, 1925). No success was reached in attempts to correlate the methanation activity of metals with their effectiveness in hydrogenation and their ability to form hydrides, carbonyls or carbides.

Fischer *et al.* (1925) proved that methane is almost the only product formed from CO and H_2 at atmospheric pressure on finely dispersed Ru, Ir, Rh, Ni, Co, Os, Pt, Fe, Mo, Pd and Ag. Hydrogenation of CO to higher hydrocarbons was found by Fischer and Tropsch (1926a) to occur at atmospheric pressure and elevated temperatures on suitably promoted Co, Fe and Ni. Pichler and co-workers discovered conditions under which ruthenium worked as an excellent catalyst for synthesis of long-chain hydrocarbons (Pichler and Buffleb, 1940). Methane was found to be the only product formed from CO and H_2 even on F–T catalysts provided the reaction temperature was sufficiently high (Fischer and Tropsch, 1926a). This suggests that the initiation step both in methanation and F–T synthesis might be identical, the only difference between the two reactions consisting in the relative rates of the chain propagation and termination.

Even as early as 1909, Mayer and Henseling observed that methane was produced by hydrogenation of carbon pre-formed on the surface of iron by decomposition of CO (Fischer *et al.*, 1925). This pointed to the possibility that surface carbon is a direct intermediate in hydrocarbon synthesis.

The early hypotheses on the formation of hydrocarbons from CO and H_2 were formulated in the first decades of the present century, when knowledge of the nature of adsorbed species was still little advanced. Chemisorption bonds were essentially identified with the corresponding bonds in the bulk: the metal–hydrogen bond was compared to hydridic bond, chemisorbed CO was identified with carbonyls, surface carbon and oxygen with carbides and oxides, respectively. The formulation of the reaction mechanism in the first report of Fischer and Tropsch (1926a) on the low-temperature synthesis of higher hydrocarbons, however, already suggested a difference between ordinary bulk carbides and surface carbides formed from CO in the fed synthesis gas. Namely, CO was postulated to decompose on the surface into surface carbides more rich in carbon than the ordinary bulk carbides; one metal atom in the surface was supposed to bind at least one carbon atom. It should be noted, however, that dissolution of bulk carbides in concentrated acids can also lead to the formation of hydrocarbons. This fact, which was known to Fischer and Tropsch (1926a), has recently been dealt with anew by Ritschel and Vielstich (1980) as a possible clue to the mechanism of hydrocarbon synthesis.

Fischer and Tropsch (1926a) further speculated that the surface carbides formed undergo hydrogenation into surface methylene groups $(CH_2)_S$. Such groups had been suggested as intermediates in ethylene synthesis by Orlov (1908), and in methane synthesis by Medsforth (1923).

Propagation of the chain was envisaged by Fischer and Tropsch (1926a) as linking up (polymerization) the $(CH_2)_s$ groups. The chain growth was terminated by hydrogenation of the end methylene group.

Fischer and Tropsch (1926a) postulated that a fundamentally different mechanism operates in the hydrogenation of CO at low pressures (formation of higher hydrocarbons) and at high pressures (formation of methane and of alcohols and further oxygenates). In their first papers (1926a), Fischer and Tropsch stated that no oxygenated products were formed in their low-pressure synthesis under optimal conditions. In the subsequent polemic with Elvins and Nash (1926a, b; Nash, 1926; Elvins, 1927), Fischer and his co-workers (Fischer and Tropsch, 1926b, 1928; Fischer and Koch, 1932, Koch *et al.*, 1935) admitted that at conditions not optimal for hydrocarbon synthesis, some oxygenated compounds can appear in the products, allegedly through unimportant side reactions due to unreduced surface oxides, or through a secondary reaction of the formed alkenes (Koch *et al.*, 1935). They even contemplated some yet unknown 'oxygenated carbides' as possible intermediates (Fischer and Tropsch, 1926b).

Further experimental studies enabled Fischer and his co-workers to identify the synthesized products in greater detail and to reformulate some of their views. A modified concept of the initiation step in the low-pressure synthesis was presented by Fischer and Koch (1932). The authors postulated non-dissociative adsorption of CO and H_2 on the catalyst surface as the initial step. On the most active centres, surface carbon (surface carbide in the terminology of Fischer and co-workers) is subsequently formed by a bimolecular reaction of the adsorbed CO either with suitably activated hydrogen (on Co and Ni), or with another molecule of Co (on Fe). The surface carbon is then hydrogenated to $(CH_x)_s$ surface species ($x = 1, 2, 3$). The oxygen formed is removed from Co and Ni catalysts predominantly as H_2O, and from Fe catalysts mainly as CO_2. For the case of $(CH_2)_s$ species one thus can write:

$$CO + 2H_2 \rightarrow -CH_2- + H_2O \text{ (on Co and Ni)}$$
$$2CO + H_2 \rightarrow -CH_2- + CO_2 \text{ (on Fe)}$$

Polymerization of the $(CH_2)_s$ species results in a range of hydrocarbon products. Long chains can undergo hydrocracking into shorter ones.

The hypothesis of Fischer and his co-workers on carbide (surface carbon) intermediates in the low-pressure synthesis of hydrocarbons was supported by the following evidence:

1. Only metals that formed carbides from CO at about 200°C were found to be active catalysts for the synthesis.
2. These catalysts exhibited activity at temperatures at which their carbides were stable.
3. The rates of carbide formation and of the hydrocarbon synthesis did not differ greatly.
4. When CO was passed over the catalysts at elevated temperatures, carbon was actually found on the surface.

(*b*) *The theory of Craxford and Rideal*

Further important development in the mechanistic conceptions of F–T synthesis was due to Craxford (1939) and Craxford and Rideal (1939). They found in experiments on a cobalt catalyst among others that

1. CO disproportionation $2CO \rightarrow CO_2 + C_s$ occurred, and the latter species was readily hydrogenated into methane with some admixtures of ethane and possibly of higher hydrocarbons.
2. The most rapid reaction in the system was the hydrogenation of CO.

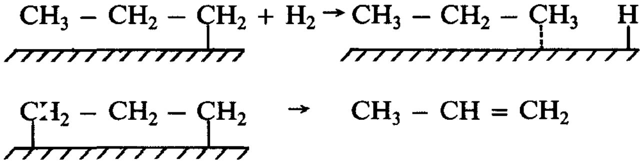
The rate of surface carbide formation from CO was observed to be clearly lower than the rate of formation of liquid hydrocarbons. This was accounted for by postulating a surface carbide (not further specified) formed much more rapidly by hydrogenation of adsorbed carbon monoxide than by disproportionation. The steps of the synthesis mechanism (Craxford and Rideal, 1939) can be presented as follows:

1. Non-dissociative chemisorption of CO to give $(CO)_s$.
2. Reduction of $(CO)_s$ to surface carbide: $(CO)_s + H_2 \rightarrow C_s + H_2O$ (the authors did not specify unambiguously whether the molecular hydrogen reacted in the adsorbed state).
3. Secondary formation of CO_2 by water-gas shift reaction $(CO)_s + H_2O \rightarrow CO_2 + H_2$ on the non-carbided portion of the surface.
4. Reduction of the carbide to chemisorbed methylene groups: $C_s + H_2 \rightarrow (CH_2)_s$.

5a. Provided the coverage of the surface by carbide and $(CH_2)_s$ groups is not large, dissociative chemisorption of hydrogen can occur on the non-carbided portion of the surface. Hydrogen atoms then convert methylene groups to methane.

5b. In the opposite case, only few hydrogen atoms are available on the surface, and the $(CH_2)_s$ groups associate to adsorbed polymethylene chains. Ultimately, when the surface is fully covered with carbon and $(CH_2)_s$ groups to the complete exclusion of chemisorbed hydrogen, the synthesis will cease and the catalyst will be choked with waxes as there is no means left for removing them from the surface. Hence, the reaction of the $(CH_2)_s$ species with hydrogen atoms yields methane, while their polymerization and reaction with molecular hydrogen leads to higher hydrocarbons.

6. The adsorbed chain formed in Step 5b is disrupted by molecular hydrogen. If much hydrogen is available, the fragments are short, and conversely.
7. Desorption of the fragments of alkanes and alkenes from the surface occurs as



$$CH_3-CH_2-CH_2 + H_2 \rightarrow CH_3-CH_2-CH_3 \quad H$$

$$CH_2-CH_2-CH_2 \rightarrow CH_3-CH=CH_2$$

8. Branched hydrocarbons are formed by incorporation of a chemisorbed carbide into chains of methylene groups.

An increase in pressure leads to the appearance of oxygenated products. Craxford sought an explanation in reactions assumingly involving carbon monoxide held in the second and outer adsorption layers.

Craxford and Rideal formulated their theory for the cobalt catalyst under study. The theory turned out, however, to be compatible with other results too, and stimulated numerous further attempts to elucidate the mechanism of F–T synthesis.

The experiments of Eidus and Zelinsky (1942) with a cobalt catalyst were consistent with the secondary formation of CO_2 suggested by Craxford and Rideal (Step 3). Kölbel and Engelhardt (1950a) showed that on iron catalysts the adsorbed $(CO)_s$ also reacted primarily with hydrogen (Step 2). On the other hand, production of CO_2 instead of H_2O can also be achieved with cobalt catalysts provided the feeding rate and the CO/H_2 ratio are sufficiently high. Thereby carbon is removed from the surface. Another important factor is temperature. Cobalt catalysts work at approximately 450 K, and the water formed does not further react at that temperature. When the temperature of the working cobalt catalyst is raised to about 510 K, the rate of the water–gas shift reaction is only slightly lower than on the metallic cobalt surface. Iron catalysts work at about 500 K and the water formed reacts almost completely with $(CO)_s$ to give CO_2.

The Steps 6 and 5a of the Craxford and Rideal hypothesis involve occurrence of molecular and atomic hydrogen on the carbided and non-carbided portions of the surface, respectively. The two portions of the surface thus play a different role in the synthesis. This idea was adopted by Fischer and Pichler (1939) as a rationale for Fischer's view that methane and higher hydrocarbons are formed through entirely different mechanisms (Fischer, 1938). According to this view, methane arises via intermediate hydrides. Competition between CO and H_2 for surface sites, i.e., competitive formation of carbides and hydrides, thus accounts for the prevailing formation either of higher hydrocarbons or of methane on various catalysts, respectively.

Herington and Woodward's (1939) results were compatible with the concept that the surface carbide on cobalt catalysts gives rise to $(CH_2)_s$ groups which polymerize into long-chain hydrocarbons, whereas the bare cobalt surface is responsible for the release of the observed products from the surface through the agency of hydrogen.

One of the debatable points of the Craxford mechanism was the speculation that first polymethylene macromolecules arise on the surface, and are subsequently hydrocracked to the final products. The physical background of this approach was questionable, although its mathematical treatment in terms of a thermodynamic polymerization–depolymerization equilibrium could reproduce the observed product distribution (Montgomery and Weinberger, 1948). Therefore, the approach of Herington (1946), who considered the chain lengthening as stepwise addition of one-carbon units (in particular, of methylene groups), was largely accepted. Mathematical treatment of this physically sound conception in terms of relative probabilities of the chain propagation and termination led to a fair agreement with the experimental product distribution which was later shown to be of the so-called Schulz–Flory type (*see* below).

(*c*) *Criticism of the carbide hypothesis*

The development of views on the mechanism of F–T synthesis up to 1948 has been summarized by Kölbel and Engelhardt (1950b).

The idea that the low-pressure hydrogenation of carbon monoxide on metals proceeds via surface carbides was publicly proclaimed by Fischer for the last time in his farewell address when he was retiring (Fischer, 1943). In Germany, Fischer's exceptional authority prevented development of any different hypotheses on the synthesis mechanism during his life (Kölbel and Hammer, 1964; Kölbel, 1977). Outside Germany, however, the carbide hypothesis had been critically examined since the very beginning. The criticism gradually strengthened, and around 1950 a wave of studies appeared, particularly in the USA and Germany, which eventually led to the general rejection of the hypothesis for some 25 years. Criticism of the carbide hypothesis was summarized by, for example, Storch *et al.* (1951), Eidus (1951) and Anderson (1956).

The first group of objections involved problems of the formation, nature and properties of the surface carbon active in CO hydrogenation. As mentioned above, Fischer and Tropsch (1926a) assumed that surface carbides formed from CO had a higher content of carbon and a lower thermal stability than bulk carbides. Bahr and co-workers found that disproportionation of CO on iron, cobalt and nickel gave rise to carbides and free surface carbon; the carbides could be hydrogenated to methane at much lower temperatures than the free surface carbon (*see* Storch *et al.*, 1951). However, cobalt catalysts were partly deactivated when carbided by CO. No appreciable amount of bulk Co_2C was formed. When complete carburization of a cobalt catalyst surface by CO and its subsequent hydrogenation at 483 K were repeated several times, a compact layer of carbon resulted, which was inactive in F–T reaction. Finally, CO above 523 K produced inactive carbon which considerably increased the surface area of the cobalt catalyst, but only slightly reduced its activity (Storch *et al.*, 1951, and references therein). Furthermore, ruthenium was found to be an efficient methanation and F–T catalyst under suitable conditions, although it does not form stable bulk carbides at the temperature of F–T synthesis. This was an important discovery, even if the possibility could not be excluded that tiny amounts of surface carbide are after all formed on ruthenium surface and act as reaction intermediate (Pichler and Buffleb, 1940; Dalla Betta and Shelef, 1977).

The uncertainty regarding the formation and role of surface carbon in F–T synthesis further increased on the strength of comparing the rates of surface carburization and F–T synthesis. The rate of carburization of a cobalt catalyst surface with CO was much lower than the rate of F–T synthesis (Eidus and Zelinsky, 1942; Eidus, 1944, 1951). The same was later reported for nickel (Ho and Harriott, 1980). Craxford (1939) suggested that the formation of surface carbon by the reaction $(CO)_s + H_2 \rightarrow C_s + H_2O$ is much more rapid than its formation by CO disproportionation. This idea was, however, rejected as allegedly unproved (Eidus, 1951). Its rejection was criticized by Braude and Bruns (1948) who pointed out the risk of identifying the rates of formation and reduction of ordinary bulk carbides with those of surface carbides.

The kinetic objections against the carbide theory seemed to be invalidated in the case of iron catalysts by the finding of Eidus (1944, 1951) that initial rates of CO disproportionation and F–T synthesis were of a comparable magnitude. Later, however, rates of CO disproportionation lower than those of F–T synthesis were observed even with iron catalysts (Braude and Bruns, 1948; Matsumoto and Bennett, 1978).

This controversy raised serious doubts whether formation of surface carbon really is indispensable for F–T synthesis, and suggested that surface carbon might only be a side product of minor role, or even act as a catalytic poison.

Important results were further obtained with catalysts precarburized by ^{14}CO. The surface carbon ^{14}C formed on iron catalyst appeared in the synthesized hydrocarbon products to a limited extent only. Therefore, the mechanism of hydrocarbon production by carbide reduction was stated to play only a minor role in the conditions of the performed experiments (Kummer *et al.*, 1948). However, formation of an *active* form of surface carbon that could act as a reaction intermediate was not ruled out. Such a possibility was also pointed out by Weller *et al.* (1948) and Anderson *et al.* (1949), who rejected *stable* carbides as intermediates in

F–T synthesis. In fact, thermodynamic calculations have shown that stable carbides can yield but very small amounts of higher hydrocarbons by hydrogenation (Hamai, 1941; Kummer *et al.*, 1948). However, in the presence of CO entailing exothermic formation of water, higher hydrocarbons are thermodynamically accessible. Kölbel and Engelhardt (1950a, b) refused bulk carbides and other defined compounds as intermediates in F–T synthesis and proclaimed formation of some active form of surface carbon for the first step in F–T synthesis.

The fact that passing hydrogen over carburized catalysts yielded mainly methane and only few higher hydrocarbons (Smith *et al.*, 1930; Eidus and Zelinsky, 1942; Kölbel *et al.*, 1949; Pichler and Merkel, 1950) was taken—though rather unjustly—as further evidence disproving the carbide hypothesis.

Other objections against the carbide theory originated in the finding that some oxygenated compounds were formed together with hydrocarbons in F–T synthesis. The amount strongly depended on the reaction conditions and the nature of the catalyst, and ranged from less than 1% in the optimum experiments of Fischer and co-workers (Koch *et al.*, 1935) to more than 10% with some iron-based industrial catalysts. Secondary formation of oxygenates from alkenes was suggested as a possible explanation by Koch *et al.* (1935) and Brötz (1949). However, the postulate advanced by Elvins and Nash (1926a) was given more credit, namely that a surface species containing atoms of carbon, oxygen and hydrogen is formed from $(CO)_s$ and hydrogen, and acts as a common intermediate both for hydrocarbon and oxygenated products.

The present state of our knowledge allows us to offer a plausible interpretation of the outlined, often contradictory observations and arguments and to reconcile them satisfactorily with the concept of the determining role of active surface carbon C_s as an intermediate in F–T synthesis and methanation (*see*, for example, Ponec, 1983). But this was not the case around 1950. At that time, doubts about the validity of the carbide theory of Fischer and his school increased to such a degree that the theory was generally rejected. The hypothesis of oxygenated intermediate became dominant in the mechanistic schemes of carbon monoxide hydrogenation. Only in the second half of the seventies was the carbide theory revived (*see* Section 5).

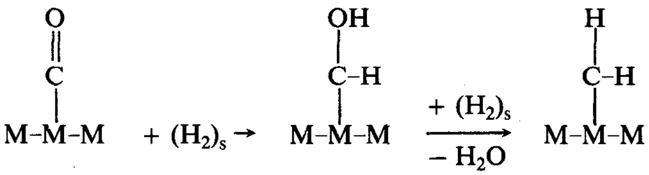
4. HYPOTHESIS OF OXYGENATED INTERMEDIATE

(*a*) *Enolic and alcoholic surface complexes*

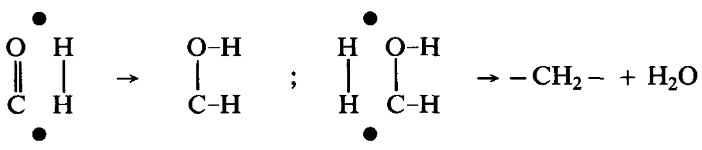
(*i*) *Early suggestions on the formation of primary complex*

Shortly after Fischer and Tropsch (1926a) announced the low-pressure synthesis of hydrocarbons from CO and H_2 and proposed its mechanism involving carbide intermediate, Elvins and Nash (1926a, b), Nash (1926) and Elvins (1927) reported that oxygenated compounds were produced along with hydrocarbons in CO hydrogenation over their Co–Mn–Cu catalyst. On the strength of this finding, they postulated that hydrocarbons and oxygenates might have a common oxygenated surface intermediate of alcoholic nature (methanol, or even higher alcohols), whose dehydration and subsequent hydrogenation leads to hydrocarbons. This hypothesis was rather similar to the earlier speculation of Medsforth (1923) that methanation proceeds via an intermediate H_2CHOH whose dehydration gives a species: $\underset{-}{CH_2}$ which is in turn hydrogenated into CH_4.

The structure of the assumed oxygenated intermediate was at first proposed but speculatively. A variety of tentative suggestions were presented. However, Hamai (1941) referred to then available kinetic and thermodynamic data and argued that hydrogenation of CO runs through a surface complex $(HCOH)_s$:



The formed surface methylene groups polymerize, and subsequent hydrogenation eventually gives rise to hydrocarbons. The proposed mechanism thus represents a connection of the initiation step involving formation of an oxygenated intermediate $(HCOH)_s$, with the propagation step consisting in polymerization of the surface methylene groups. A similar approach was presented later by Eidus and Zelinsky (1942), Eidus (1943), and Myddleton (1944). Eidus (1943) explained his kinetic results in terms of Balandin's multiplet theory of catalysis. He assumed that a $(HCOH)_s$ complex forms by addition of adsorbed molecular hydrogen to the neighbouring adsorbed carbon monoxide, and that this complex reacts with another adsorbed hydrogen molecule to give water and an adsorbed methylene group:



Surprisingly, the possibility that $(HCOH)_s$ could disintegrate into water and surface carbon was not mentioned by the author.

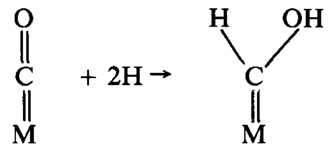
The concept of the primary oxygenated complex $(HCOH)_s$ was largely accepted. In some of its modifications (Hamai, 1941; Storch *et al.*, 1951), gradual addition of adsorbed hydrogen atoms rather than of hydrogen molecules was considered.

(*ii*) *Mechanism of chain growth and termination*

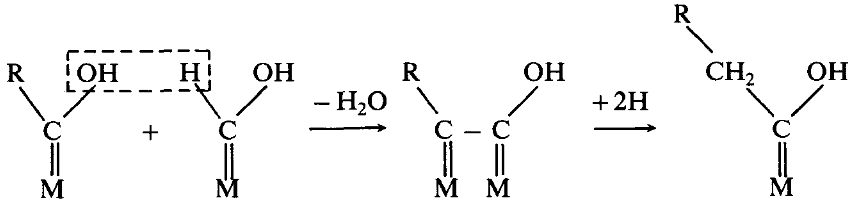
The mechanism suggested by Hamai (1941), Eidus (1943) and others considers the formation of the surface complex $(HCOH)_s$ as the last common step in the synthesis of hydrocarbons and of alcohols from CO and H_2. In the next step, bifurcation into routes leading to hydrocarbons and to alcohols was assumed. In the former route, $(CH_2)_s$ groups arise and polymerize into a chain.

Storch *et al.* (1951) postulated a mechanism which postponed the above-mentioned bifurcation until the terminal steps of the synthesis, when the chain build-up had been completed. Chain propagation was suggested as condensation of a C_1 enolic surface species $M = C(OH)H$ with another enolic or an alcoholic surface species under elimination of water. The postulated mechanism can be presented as follows:

Chain initiation.

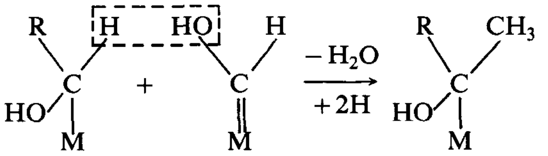


Chain propagation. The main pathway involves condensation at the end (α) carbon atom followed by hydrogenation:



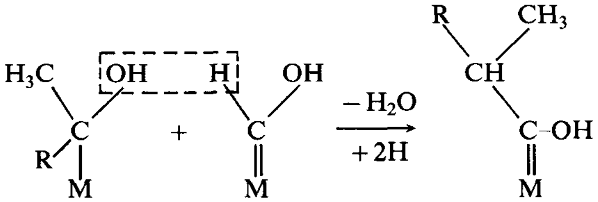
(I)

A part of the enolic species $M=C(OH)R$ can, however, be hydrogenated to alcoholic species $M-CH(OH)R$. Then, along with the pathway (I) involving two enolic species, an alternative process involving an alcoholic species can take place as



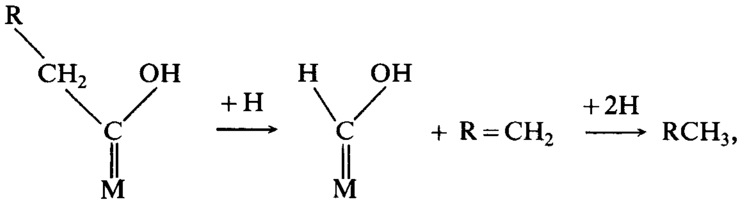
(II)

In this way a β-carbon (adjacent-to-end carbon) hydroxyl group is formed, and its attack by $M=CHOH$ leads to branching of the chain:



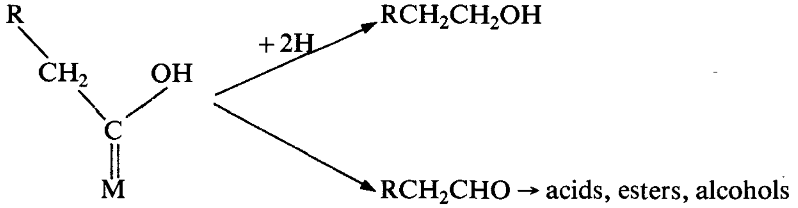
(III)

Chain termination. The chain growth is terminated either by formation of hydrocarbons under regeneration of the enolic species $(HCOH)_s$:



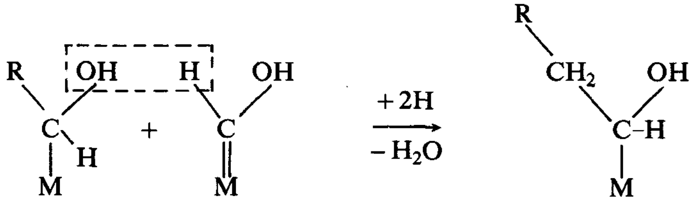
(IV)

or by formation of oxygenated products, with or without involvement of hydrogen:

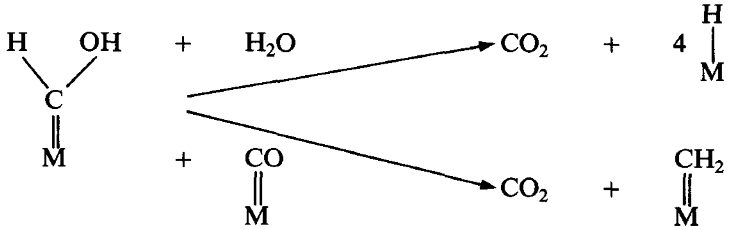


(V)

Kummer and Emmett (1953) and Hall *et al.* (1960), referring to the experiments with addition of radioactively labelled alcohols into the $CO + H_2$ mixture over iron catalysts, modified propagation step (I) by suggesting that the enolic species M = C(OH)H undergoes condensation with the alcoholic species M–CH(OH)R rather than with the enolic species M = C(OH)R:



They also replaced the termination step (IV) by a postulate of direct formation of alkanes and alkenes through hydrogenation and dehydrogenation. Furthermore, an alternative conversion of the enolic complex M = C(OH)H into CO_2 was proposed:



The upper reaction replaces the usual water–gas shift reaction $CO + H_2O \rightarrow CO_2 + H_2$. The lower reaction represents primary production of CO_2 without involvement of water and direct formation of alkenes.

Mathematical treatment of the product distribution resulting from the chain build-up through addition of C_1 increments (irrespective of whether they contain oxygen or not) leads to equations (Storch *et al.*, 1951) which have later been shown as equivalent to the so-called Schulz–Flory equation for molecular weight distribution in polymerization processes (Henrici-Olivé and Olivé, 1976; Madon, 1979).

The observed occurrence of branched hydrocarbons in the synthesis products could be accounted for in terms of the suggestion (Storch *et al.*, 1951; Kummer and Emmett, 1953) that the chain growth by attachment of carbon atoms takes place in approximately 90% on α-carbon and only in about 10% on β-carbon (Hall *et al.*, 1960). Mathematical treatment led to a two-parameter equation describing the distribution found (Storch *et al.*, 1951). Chain-growth schemes accounting for the product distribution have been dealt with in a number of other papers (e.g., Pichler *et al.*, 1967; Schulz, 1977; Novak *et al.*, 1982). To account for ethyl isomers next to methyl-substituted carbon chains, more complex schemes including a third constant have been advanced (Anderson and Chan, 1979). Generally, C_1 and C_2 fractions deviate to some degree from the Schulz–Flory distribution. These and many other deviations from the Schulz–Flory distribution have been thoroughly discussed and their possible reasons dealt with by Jacobs and Wouwe (1982).

The enolic complex able to initiate chain growth need not necessarily be the $M=C(OH)H$ species formed from CO and H_2, but can also arise from adsorbed alcohols (Kummer and Emmett, 1953) and aldehydes (Hall *et al.*, 1960). On the other hand, surface complexes which have one or more carbon atoms and act as chain initiators need not be identical with complexes acting in chain propagation (Kummer and Emmett, 1953; Schulz, 1977).

The ability of reactive products (alkenes, alcohols, aldehydes, etc.) to participate in chain initiation or propagation is not conditioned by formation of an enolic intermediate. Ethylene, and even some other alkenes can be incorporated into chains (Hall *et al.*, 1960; Gibson and Clarke, 1961; Schulz, 1977; Dwyer and Somorjai, 1979). However, secondary involvement of desorbed alkenes in chain growth is practically negligible under usual conditions of F–T synthesis. The main reaction of alkenes is their hydrogenation to give alkanes.

(*iii*) *Attempts to provide supporting evidence*

A number of attempts have been undertaken to infer some information on the formation, structure and properties of the suggested oxygenated intermediates in F–T synthesis. Adsorption behaviour of alcohols and other compounds related to the presumed intermediates, as well as interaction of CO and H_2 under conditions atypical for F–T synthesis have been studied.

Behaviour of alcohols and aldehydes. Methanol was the most widely studied compound in this respect. In general, methanol undergoes decomposition on metal surfaces, sometimes even at room temperature. Studies of the methanol behaviour on metals encompassed determination of the rate and activation energy of methanol decomposition (Eidus, 1943; Gall *et al.*, 1952; Gibson, 1953; Darby and Kemball, 1957); infrared spectra of adsorbed methanol (Blyholder *et al.*, 1976, and references therein); thermal desorption of methanol (Goodman *et al.*, 1978); addition of radioactively labelled methanol to the synthesis gas feed (Kummer and Emmett, 1953; Hall *et al.*, 1957). These experiments provided much interesting information, but failed to indicate definitely whether a complex active in hydrocarbon synthesis can be formed from methanol at all, and if so what is its nature.

Higher alcohols disintegrate on the catalyst surface to a limited extent. Some intermediate formed from them probably participates in the build-up of hydrocarbons on iron (Gall *et al.*, 1952; Gibson, 1953). As for cobalt, these authors arrived at a contradictory conclusion to that of Emmett and his co-workers (e.g., Hall *et al.*, 1960).

Similarly, experiments with formaldehyde and higher aldehydes did not sufficiently clarify the question of the possible participation of aldehydes in hydrocarbon synthesis (Gibson, 1953; Hall *et al.*, 1957, 1960).

Behaviour of ketene and diazomethane. Addition of ketene ($H_2C=C=O$) labelled with ^{14}C either in the CH_2-group (Blyholder and Emmett, 1959) or in the CO-group (Blyholder and Emmett, 1960) into the mixture of CO and H_2 passed over iron catalyst showed that ketene was adsorbed preferentially, decomposed mainly into $(CH_2)_s$ groups and CO, and the $(CH_2)_s$ groups efficiently initiated hydrocarbon chains. Reconsideration of the original interpretation of the above-mentioned experiments has recently led to the conclusion that the $(CH_2)_s$ groups also participate in chain propagation (Ponec and van Barneveld, 1979; Biloen and Sachtler, 1981; Ponec, 1983). Adsorbed ketene is hydrogenated to a small extent before decomposition and this gives rise to the major part of the ethane produced. On the other hand, ethylene is formed mainly from the methylene precursor. CO from ketene is more readily incorporated into the chain than CO supplied in synthesis gas. Also over cobalt catalyst, a mixture of ketene and hydrogen gave typical products of F–T synthesis (Warner *et al.*, 1946).

It is worth noting that Blyholder and Emmett (1959) in their mechanistic considerations hypothesized that CO is attached to the surface both by the carbon and the oxygen atom. This idea has later reappeared in reaction schemes of various authors (*see* below).

Hydrocarbons were also obtained from mixtures of diazomethane (H_2CN_2) and hydrogen (Brady and Pettit, 1980), and of diazomethane and synthesis gas (Brady and Pettit, 1981) over cobalt, iron, ruthenium and even nickel. Diazomethane alone yielded chiefly ethylene.

The above-mentioned experiments showed that $(CH_2)_s$ species could efficiently initiate and propagate hydrocarbon chains. However, no clear-cut elucidation was obtained for the origin of the $(CH_2)_s$ groups, i.e., whether they were formed by hydrogenation of surface carbon C_s, or by hydrogenation of a $(HCOH)_s$ complex with elimination of water. Moreover, the possible chain growth from one-carbon oxygenated species without involvement of $(CH_2)_s$ units was neither definitely proved nor excluded.

Interaction between CO and H_2 under various conditions. In order to elucidate the first step in hydrogenation of carbon monoxide, a number of studies using a variety of experimental techniques were performed on the CO–H_2–metal systems at low temperatures and very low equilibrium pressures. The results obtained, however, did not show any direct relevance to CO hydrogenation. In most cases, only non-specific positive interaction between adsorbed carbon monoxide and hydrogen was noted. When some defined complex appeared to form, it disintegrated well below the temperature of F–T synthesis.

Of greater relevance are studies of the interaction between CO and H_2 over industrial catalysts at atmospheric or higher pressure, but at temperatures lower than are those at which hydrogenation of CO sets in. The results show a positive interaction leading to increased adsorbed amounts of both gases. Their ratio is near unity; formation of an unstable complex with a H_2:CO ratio of 1 appears to be likely (Vannice, 1976).

The increased amount of adsorbed CO in the presence of hydrogen can be accounted for by the change of the bridge-bonded CO requiring two sites into the linear form which needs but one site (Wedler *et al.*, 1975; Andersson and Pendry, 1978; Silverman *et al.*, 1980), or by the formation of surface complexes of CO and H_2 (Blyholder and Neff, 1962; Huang and Richardson, 1978). The mass spectra of products desorbed from iron catalyst over which pulses of CO were injected into a stream of H_2 under reaction conditions were interpreted in terms of the formation of formaldehyde, and hence involvement of an enolic surface intermediate $(HCOH)_s$ was proposed (Kölbel and Hanus, 1974). An aldehydic surface complex with H_2:CO ratio of 1 was inferred from the interpretation of infrared spectra measured with iron catalyst under reaction conditions (Kölbel *et al.*, 1970). Occurrence of enolic species $(HCOH)_s$ was suggested from thermal gravimetric studies with a Ni/Al_2O_3 methanation catalyst in a mixture of $CO + H_2$ at 473 K (Farrauto, 1976).

However, none of the studies of the kind mentioned provided indisputable evidence on the nature of the surface complex formed and its bonding to the surface. The complex need not be a defined species and may represent merely attachment of CO and H_2 to the same surface centre (Vannice, 1976).

Results of numerous kinetic studies have been consistent with the concept of a $(H_2CO)_s$ surface intermediate bonded to one or two surface sites. A variety of kinetic models have been proposed for methane formation on metal surfaces (Vannice, 1976). They differ from each other in the sequence of the reaction steps and in the identification of the rate-determining step. The simplest appears to be the model of Vannice (1975). It assumes that the surface is predominantly covered by non-dissociated CO which interacts with the adsorbed hydrogen, and that the rate-determining step is the reaction of this $(H_2\text{-}CO)_s$ complex with hydrogen to form water and a $(CH_x)_s$ moiety. Recently, Vannice and co-workers reconsidered the above scheme and replaced it by a reaction model which involves no assumption regarding CO coverage and suggests CH_4 formation from surface carbon produced by a hydrogen-assisted dissociation of CO (Wang *et al.*, 1981).

Some recent studies of the kinetics of methanation involving the assumed $(H_2CO)_s$ intermediate are referred to in papers by Huang and Richardson (1978) and Ho and Harriott (1980).

Again, kinetic studies have not been able to provide adequate proof that an oxygenated intermediate is formed in the hydrocarbon synthesis from CO and H_2.

(*iv*) *Parallel and consecutive reaction routes*

In the preceding sections we have mentioned that bifurcation in the carbon monoxide hydrogenation into the routes producing hydrocarbons and oxygenates was assumed by different authors to occur at different stages of the reaction.

1. Fischer's school claimed that bifurcation sets in during adsorption of CO, and that the two reaction routes are completely independent from then on (Fischer and Tropsch, 1926b, 1928; Fischer and Koch, 1932; Koch *et al.*, 1935).
2. Hamai (1941), Eidus (1943) and some others postponed the bifurcation to the reaction of the assumed intermediate $(H_2CO)_s$ or generally $(H_xCO)_s$.
3. In schemes postulating chain growth by condensation of enolic $M=C(OH)R$ and alcoholic $M\text{-}CH(OH)R$ species, the bifurcation was proposed to take place only in the termination step (Storch *et al.*, 1951; Hall *et al.*, 1960).

Similar to the latter concept, Warner *et al.* (1946) suggested that the surface intermediate is adsorbed ketene $R-CH=C=O$. This is lengthened by addition of $(CH_2)_s$ units, and in the termination step either undergoes hydrogenation into alcohols and aldehydes, or hydration into acids, or releases CO and yields alkenes. Brötz (1949) suggested that chain growth by stepwise addition of $(CH_2)_s$ groups (said to arise from CO and H_2 in a single step without involvement of surface carbon) is terminated by saturating free valencies with hydrogen; methyl groups, water or $(OH)_s$ groups; or their thermal cancellation to give straight-chain alkanes; α-methyl branched alkanes; alcohols; and alkenes, respectively.

Chain branching has been ascribed to various stages in the synthesis of hydrocarbons and alcohols. The differentiation between alkanes and alkenes, however, has generally been placed at the termination stage. In some systems at least, alkenes are the dominant primary products and it is only at their readsorption when alkanes are formed (Schulz, 1977; Dwyer and Somorjai, 1978; Kelley and Goodman, 1982; and references therein). However, addition of labelled alcohols into the synthesis gas fed to iron catalyst resulted in higher radioactivity of alkanes compared to the corresponding alkenes, at least for shorter chains (Kummer and Emmett, 1953; Hall *et al.*, 1957, 1960; Kokes *et al.*, 1957). This can be taken as indicative of two competing parallel propagation routes. One route would lead predominantly to alkenes (which can undergo hydrogenation to alkanes), the other route would produce at least partly alkanes as primary products. In the latter route, the contribution of the labelled alcohol was found to be more significant than in the former one. This suggests that oxygenated intermediates might be involved. Hence, one could expect that alcoholic intermediates lead primarily to alkanes. Anyway, the former route prevailed under the given conditions, even with adsorbed alcohols, suggesting that oxygen-free intermediates of alkyl nature predominated.

Attempts have been made to organize the wealth of results obtained under various conditions by formulating rather complex reaction schemes with interconnections and crossings, able to unify and account for all the experimental findings. Such networks of mechanistic steps certainly help to illuminate the reactions involved—at least potentially—in F–T synthesis, but on the other hand their cognitive value for particular cases is somewhat invalidated because of their rather general nature.

A scheme claiming some generality was proposed by Kryukov *et al.* (1961). The authors postulated that the first step in F–T synthesis is formation of a $(HCOH)_s$ species, which partly converts into $(CH_2)_s$ and $(H_2COH)_s$ species, and partly participates in the chain growth. The growth is assumed to proceed through four potential ways:

1. Linking of $(CH_2)_s$ species leads to alkenes and alkanes.
2. Stepwise incorporation of $(CH_2)_s$ units into $(HCOH)_s$ species leads to alcohols.
3. Addition of $(HCOH)_s$ species to polymethylene chain provides $(RCHOH)_s$ species which can further grow by condensation with $(H_2COH)_s$ intermediates to give both alcohols and hydrocarbons.
4. Polycondensation of $(H_2COH)_s$ and $(RCHOH)_s$ species leads again both to alcohols and hydrocarbons.

Furthermore, combination of longer chains with or without oxygen may act in chain propagation. The actual importance of the particular routes is given by the probability ratio of the hydrogenation and condensation of $(HCOH)_s$ species, which depends on the catalyst used and on the conditions. The scheme does not include the mechanism of CO insertion. Today, it is mainly of historical interest only.

Rofer–DePoorter (1981) has presented a very complete mechanistic scheme for CO hydrogenation, starting with the adsorption of CO and H_2, and summarizing ideas suggested on the elementary reactions involved. The scheme includes 55 steps, all of them documented by some direct or indirect experimental evidence or at least by analogy to homogeneous cluster reactions. Clearly, only a fraction of the alternatives is operative under particular conditions. It appears likely that still other reaction steps or even pathways will be disclosed as important under some specific circumstances.

(*b*) *Insertion of CO into metal-alkyl and metal-hydrogen bond*

(*i*) *Insertion in the heterogeneously catalysed CO hydrogenation*

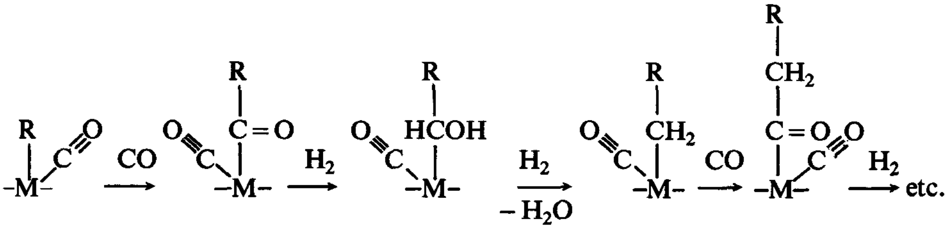
At present there is no doubt that the build-up of hydrocarbons as well as oxygenates in carbon monoxide hydrogenation occurs predominantly via C_1 units. The role of other incorporating species such as alkenes is considered as marginal only. Linking up of surface methylene groups $(CH_2)_s$, and condensation of the C_1 enolic species $M = C(OH)H$ with another enolic or alcoholic surface intermediate have been widely discussed and analysed in a number of studies. Both these approaches imply that the respective C_1 units are preformed on the surface. They do not, however, explain the abrupt fall in the formation of higher hydrocarbons immediately after the $CO + H_2$ mixture has been switched to pure hydrogen; nor do they account for the predominant production of methane from reactive surface carbon when its concentration exceeds that one prevailing at the conditions of F–T synthesis. These observations indicate that the presence of CO is possibly of major importance for chain propagation.

Karzhavin (1947) speculated that $(CO)_s$ is needed to link two $(CH_2)_s$ species together, whereby $(HC = C = CH)_s$ intermediates arise which are subsequently hydrogenated to give alkenes and alkanes. The author assumed for his $Ni - MnO - Al_2O_3$ catalyst that the $(CH_2)_s$ groups are on Ni-sites, while the $(CO)_s$ are on MnO-sites. Still earlier, Pichler and Buffleb (1940), when working on the ruthenium-catalysed synthesis of high-molecular alkanes, pointed out the possible participation of the molecular carbonyl-like adsorbed $(CO)_s$ in the synthesis of higher hydrocarbons. The authors drew attention to two facts:

1. Partial pressure of CO and temperature optimum for F–T synthesis over Fe, Co, Ni and Ru, are just below the respective values at which formation of volatile carbonyls becomes pronounced.
2. Of all the platinum metals, it is just ruthenium that forms carbonyls from CO and that is active in F–T synthesis.

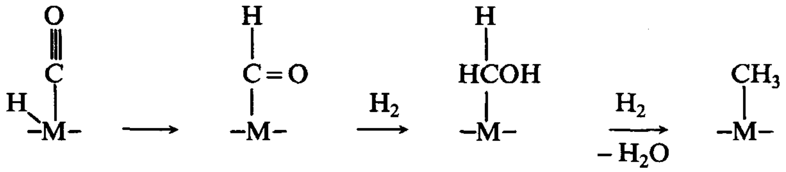
However, since formation of ruthenium carbide was not proved at synthesis conditions, the activity of ruthenium in F–T synthesis was not compatible with the carbide theory predominant in Germany at that time. Therefore, it had to be assumed that after all a very small amount of ruthenium carbide is formed as intermediate in F–T synthesis.

In 1947, Pichler emphasized anew the probable importance of metal–carbonyl type intermediates in F–T synthesis and related reactions (*see* Ref. 33 in Wender, 1976). Anderson (1956) also mentioned such a possibility. But it was Wender and his co-workers who—in their paper on carbon monoxide transfer to organometallic carbonyls by reversible insertion of a CO molecule between the metal atom and carbon—applied this idea to F–T synthesis, and suggested the following scheme for chain growth (Wender *et al.*, 1958):



In coordination complexes both the CO group and the alkyl group must be associated with the same metal atom. To obviate the possible steric difficulties in the above scheme at higher surface coverages, insertion of CO from a neighbouring metal atom was surmised.

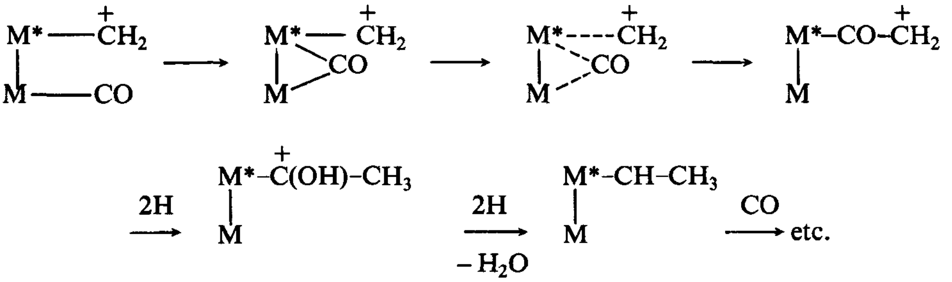
Soon after that, Sternberg and Wender (1959) offered further evidence to support the reversible insertion of CO into the $-C-M(CO)_x$ bond, and detailed its application to F–T synthesis. For the formation of the initial methyl group, with no proven analogy in the carbonyl-catalysed reactions, the authors suggested the following scheme extending the concept of CO insertion to the metal–hydrogen bond:



The experiments of Gibson and Clarke (1961) provided some support to the theory of CO insertion in hydrocarbon chain growth.

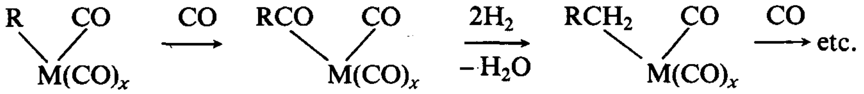
In organometallic chemistry it has been established that it is probably not CO which is inserted into the alkyl–metal bond, but rather the alkyl group which migrates from the metal to the carbon atom (Blyholder and Neff, 1966; Blyholder *et al.*, 1976; Wender, 1976). This, however, does not alter the above reaction schemes.

Roginsky (1965) proposed a modification of chain growth by CO insertion involving bridge-bonded CO and methylene groups:



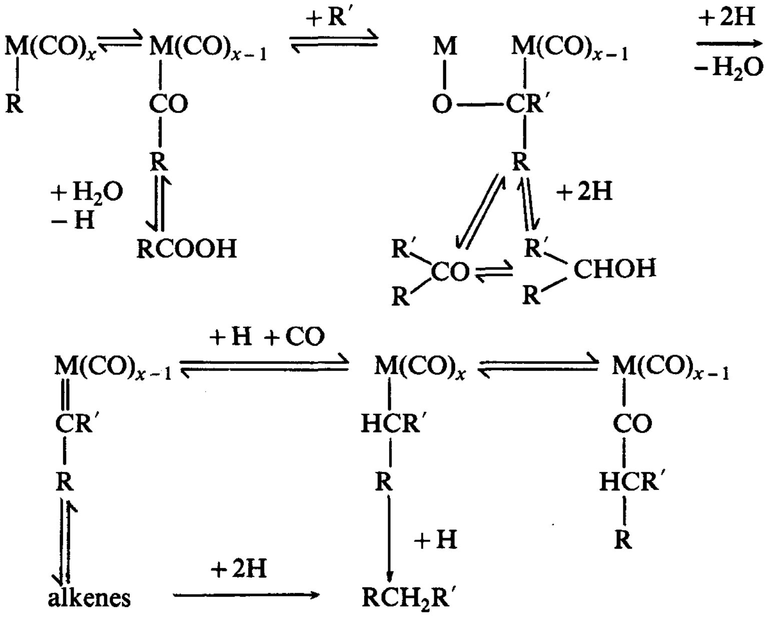
Here, M* and M denote two types of surface sites differing from each other in structure and reactivity. Several sites are claimed to form an active centre: two sites for carbon, further sites for hydrogen and for reaction products.

In contrast to Roginsky, Pichler and co-workers suggested that only one metal atom is required for the chain growth, and proposed the following scheme (Pichler *et al.*, 1964):



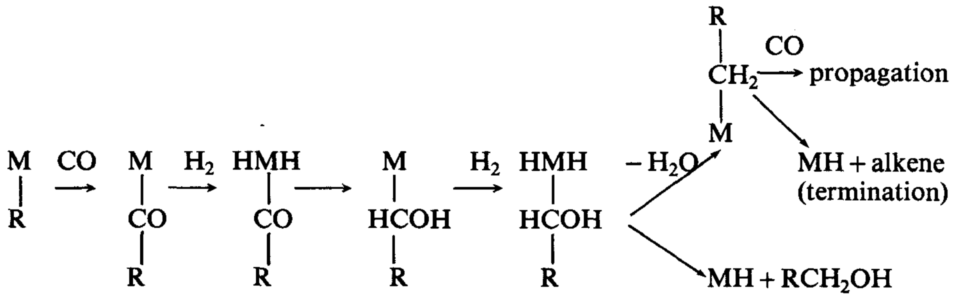
The concepts of chain growth involving only one surface atom fitted into the endeavour to establish common features of homogeneous and heterogeneous catalysis, typical for the sixties. First attempts were then made to conceive heterogeneous catalysis as coordination chemistry on the particular reaction sites. The analogy between coordination complexes and heterogeneous reactions was thoroughly investigated by Blyholder and co-workers (e.g., Blyholder and Goodsel, 1971; Blyholder *et al.*, 1976; and references therein). The authors concluded that concepts of the bonding in organometallic and coordination compounds are sufficient to account for the structure and reactions of surface species on metals. They inferred from infrared spectra that in corners, edges and dislocations of the surface are atoms with unsaturated valences, and each of these atoms can coordinate both a carbonyl and an alkyl group. The latter can then easily migrate between the carbonyl group and the metal.

Pichler's conception of the CO insertion was further developed in the paper published together with Schulz (Pichler and Schulz, 1970). They proposed a complete scheme for the formation of different products based on the reversible insertion of CO into both the metal–carbon and metal–hydrogen bond. Participation of Zein El Deen in its formulation was acknowledged. The scheme can be put in a condensed form as follows:

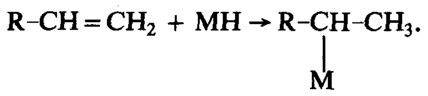


where $R = C_nH_{2n+1}$, $n = 0$, 1, etc. In the main reaction pathway, $R' = H$. The side pathway with $R' = CH_3$, followed by still at least one CO-insertion step, accounts for chain branching. Competitive adsorption of reactants, intermediates and products determines the course of synthesis and the type of products. In the scheme proposed, hydrogenation of the inserted CO runs through a complex requiring two vicinal sites, to which both its carbon and oxygen atom are coordinated. A similar complex was suggested earlier by Blyholder and Emmett (1959).

Henrici-Olivé and Olivé (1976) proposed a mechanism of F–T synthesis in which the importance of hydridization of the reactive metal centre is emphasized. It can be outlined in the following way:

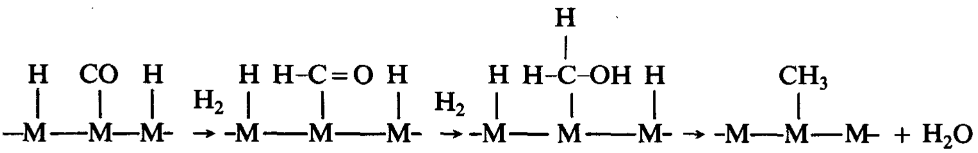


In principle, the scheme requires only one adsorption site, but is less general than that of Pichler and Schulz (1970). Alkanes are suggested to be formed by hydrogenation of alkenes. When alkenes readsorb in β-position, branching of the chain may occur:



$$R\text{-}CH{=}CH_2 + MH \rightarrow R\text{-}\underset{\displaystyle M}{\underset{|}{C}H}\text{-}CH_3.$$

Finally, Wender (1976) surmised that a number of active metal atoms are needed for the formation of the methyl group, so that the metal atom which holds the carbonyl group is surrounded by metal atoms with adsorbed hydrogen atoms:



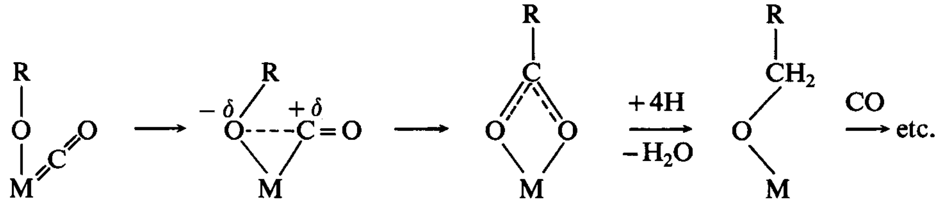
This conception represents a modification of Wender's earlier hypothesis (Sternberg and Wender, 1959) that the initiation step in F–T synthesis is formation of the M–(CO)–H complex in a way analogous to the insertion of CO into a metal–alkyl bond. Once the methyl–metal bond is formed, chain lengthening can proceed by the ordinary insertion of CO into the alkyl–metal bond.

The idea that a different mechanism operates in chain initiation and chain growth was further developed by van Barneveld and Ponec (1978). They visualized the initiation step as formation of active surface carbon through dissociation of CO (*see* Section 5(b)), with the subsequent chain growth as repeated CO insertion into carbon–metal bond on one active site. This scheme was compatible with the authors' results in experiments with Ni–Cu alloys. It was also in line with the well-known easy insertion of CO into metal–alkyl bonds in organometallic complexes (*see* Section 4(bii)).

The mechanism of van Barneveld and Ponec was adopted by other authors (Dwyer and Somorjai, 1978; Matsumoto and Bennett, 1978). Kitzelmann and Vielstich (1978) postulated a similar mechanism from their experiments with iron catalysts. They considered the initiation step as formation of active surface carbon species and their hydrogenation to $(CH_3)_s$ groups (*see* Section 5(d)). The chain propagation was regarded as the attack of $(CO)_s$ on the Fe–CH_3 bond, whereby a complex Fe–CH(CH_3)–O–Fe was formed. Such a complex was considered earlier by Blyholder and Emmett (1959) and Pichler and Schulz (1970). CO and H_2 were assumed to compete for free surface sites, and their relative coverages determine whether formation of hydrocarbons or oxygenates prevails.

A mechanism involving insertion first into M–OH bond and formation of a M–O–CH = O intermediate was proposed by Deluzarche *et al.* (1978), but the conditions of the corresponding experiments were somewhat atypical.

Blyholder and co-workers applied infrared spectroscopy to identify products of the presumed reactions of CO insertion expected to occur when a mixture of ethylene, CO and H_2 (Blyholder *et al.*, 1976), and a mixture of propanol, CO and/or H_2 (Blyholder and Shihabi, 1976) were fed to Co/SiO_2 catalyst at 373 K. The results obtained, however, pointed to a different mechanism: the migrating alkyl group is not bonded to a surface metal atom, but migrates from an alkoxide species to a chemisorbed CO molecule, and the M–C bond of the carbonyl is ruptured while M–O bond of a carboxylate group forms. This can be depicted as



The experimental evidence compatible with this proposal was limited in essence to Co only, and was not confirmed with Fe films (Blyholder and Goodsel, 1971). The possible participation of the support in the proposed scheme was not ruled out.

For the sake of completeness it should be mentioned here that formation of an alkoxide species is presumed in the reaction pathway suggested recently by Sapienza (*see* Haggin, 1981), though no CO insertion is involved. $(CO)_s$ species attached to two metal atoms through its carbon and oxygen atom is again proposed, as in the schemes of Blyholder and Emmett (1959) and Pichler and Schulz (1970). The following suggested steps involve intermediates bonded to the surface by oxygen atoms only, not by carbon atoms. Arguments in support of this unusual approach were not presented (Haggin, 1981).

In summary, no direct evidence of the CO insertion mechanism in chain growth has been provided thus far. The indirect support available (Schulz, 1977) is mainly the similarity in the bonding of chemisorbed CO and carbonyls on catalytically active metals (Ugo, 1975), and the analogy with reactions of homogeneous metal carbonyl complexes, particularly with those catalysed by $Co_2(CO)_8$. But these homogeneous processes take place at high pressures only and are slow. Moreover, metal atoms in carbonyls and in metal surfaces have different properties, the former being able to bind many more CO groups than the latter. In addition, the scheme of Pichler and Schulz (1970) was criticized in the following points (Falbe, 1977):

1. The complex $H–(CO)–M(CO)_x$ can hardly be stable at the conditions of F–T synthesis.

2. The formation of the $\begin{matrix} H_2C & — & O \\ | & & | \\ M(CO)_x & & M \end{matrix}$ species is debatable from the steric point of view, and moreover it requires a complicated transfer of electron densities.
3. The intermediate $CH_3M(CO)_x$ with the weakened alkyl-metal bond will undergo hydrogenation to methane rather than CO insertion into the weakened bond.

One can add that the required attachment of several CO groups to one metal atom is debatable. Some evidence that chains do not grow solely by CO insertion to the exclusion of other mechanisms follows from the recent findings that the formation of higher hydrocarbons continued—although at a much lower rate—even when CO was removed from the gas phase (*see* Section 5).

(*ii*) *Homogeneously catalysed reduction of CO*

Studies of metal carbonyl chemistry have been expected to assist in developing new procedures for the facile transformation of CO into hydrocarbons and organic chemicals and in understanding the ways in which existing catalysed reactions occur.

There are two fundamental types of carbon monoxide activation in homogeneous catalysis (Eisenberg and Hendriksen, 1979):

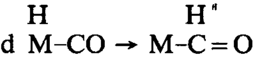
1. Reduction of the CO triple bond by interaction with two or more metal centres (Kuhlmann and Alexander, 1980).
2. A reactive charge distribution.

The former case closely relates to dissociative CO adsorption on metal surfaces; the latter consists of enhancing the reactivity of the carbonyl ligand to nucleophilic attack at carbon.

Masters (1979) has summarized the present knowledge of organometallic chemistry regarding

1. The possible initiation of the chain growth by the direct insertion of CO into a metal–hydrogen bond.
2. The problem whether one or more metal centres are necessary for the chain propagation.

Leaving apart the formation of alcohols, we will deal with the problems relating to hydrocarbons only.

First, direct insertion of CO into a metal–hydrogen bond has not been firmly established thus far. On the other hand, the carbonyl insertion into the transition metal–alkyl bond and its reverse, i.e., decarbonylation, play a key role in many reactions of organometallic chemistry. The difficult direct insertion of CO into a metal–hydride bond  $\overset{H}{M}\text{–CO} \rightarrow \overset{H}{M}\text{–C=O}$ might be accounted for by the relative strengths of a metal–hydride and metal–methyl bond (Masters, 1979). If so, the formation of a 'simple' metal–formyl intermediate  $\text{M–}\overset{H}{C}\text{=O}$ in F–T synthesis is not very probable, and mechanisms involving activation of the oxygen in the carbonyl group are more likely (*see* later).

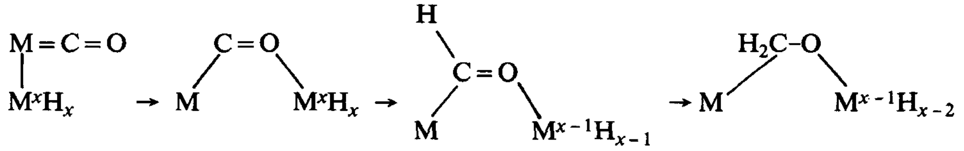
Reduction of coordinated carbon monoxide to alkyl by a variety of agents in the homogeneous phase has long been known, but the reduction achieved by molecular hydrogen was reported only considerably later. Mononuclear complexes of zirconium and titanium were used to promote this reduction, and methanol resulted. This CO hydrogenation involves hydride transfer to the carbonyl group to give a formyl species with both the carbonyl carbon and oxygen atoms coordinated to the same metal centre. Therefore, it is possible to overcome the above-mentioned unfavourable ratio of the bond strengths which impedes the direct insertion of CO into the metal–hydrogen bond. Further relevant cases of the CO reduction by hydridic species have been surveyed by Eisenberg and Hendriksen (1979).

The idea that activation of CO could be enhanced by its coordination to more than one metal centre has been developed by Muetterties (1975, 1976, 1977). Mononuclear coordination catalysts in the $H_2 + CO$ reaction with a wide range of solvents were found to be inactive (Thomas *et al.*, 1976), while polynuclear complexes of osmium and iridium catalysed the CO hydrogenation into methane and higher hydrocarbons at mild conditions of 413 K and 2 atm; the reaction rates were of course very low. However, Brenner and Hucul (1980) argue that the inability of homogeneous mononuclear complexes to catalyse the reduction of CO may be due to the inactive form of the catalysts rather than to their mononuclear nature. They found high reactivity for catalytic methanation of $Mo(CO)_6$ and $W(CO)_6$ supported on Al_2O_3. The results are consistent with the methane being produced from mononuclear species, but the possibility could not be excluded that the mononuclear catalytic species agglomerize under reaction conditions to clusters. Bradley (1979) even suggested that CO hydrogenation to hydrocarbons in solutions of the polynuclear $Ru_3(CO)_{12}$ cluster is in fact catalysed heterogeneously on the surface of Ru metal formed by the cluster breakdown.

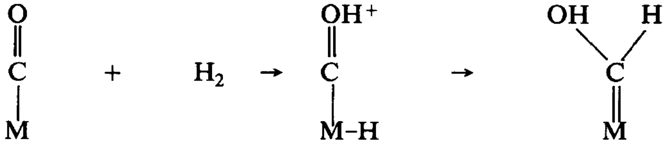
Demitras and Muetterties (1977) reported the F–T synthesis of C_2 and even higher alkanes and alkenes in homogeneous phase catalysed by polynuclear metal carbonyls in suitable media. Masters *et al.* (1979) announced a similar result with mononuclear metal carbonyls in the medium of a strong Lewis acid and an efficient hydridic donor. Finally, Henrici-Olivé and Olivé (1979) reported a homogeneously catalysed production of hydrocarbons (alkylbenzenes) with chain lengths corresponding to the Schulz–Flory distribution observed in heterogeneous systems.

The idea of Muetterties (1975) that more coordination sites than one are needed for CO hydrogenation appears to be consistent with the suggestion that the heterogeneously catalysed CO hydrogenation requires several active surface sites (*see* Section 5(e)).

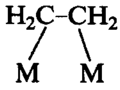
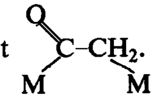
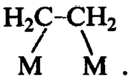
In accordance with the approach of Muetterties, Masters (1979) suggests that activation of CO toward hydrogen reduction requires its coordination via both the carbon and oxygen atoms. The carbonyl oxygen interacts with an electron-deficient site of the catalyst system, and Masters proposes two alternative mechanisms. One consists in the attack via hydridic hydrogen at the carbonyl carbon to give an aldehydic complex which undergoes further reduction; this is analogous to the scheme of heterogeneous F–T synthesis published by Pichler and Schulz (1970):



($x = 2$, or possibly 4). The second alternative involves initial attack by protonic hydrogen (formed by heterolytic splitting of hydrogen into M–H and H^+) at carbonyl oxygen, followed by hydridic attack at carbonyl carbon, to give an intermediate analogous to that advanced by Storch *et al.* (1951):



In the two initiation processes, further hydrogenation gives rise, after loss of water, to a C_1 species of carbene structure $M = CH_2$. This species may be hydrogenated to a metal–methyl species which can either be further hydrogenated to give methane (termination step) or undergo carbonyl insertion to give an acyl complex (propagation step). Masters (1979) suggests still two other reactions. When two carbene species are formed in close proximity to each other, they can dimerize to


$\begin{matrix}H_2C-CH_2\\ / \quad \backslash \\ M \qquad M\end{matrix}$ which could further give ethylene and finally ethane or metal–ethyl. Alternatively, if the carbene intermediate may be viewed as nucleophilic, it could attack the carbonyl carbon of an adjacent carbonyl group to give a ketone-like C_2 unit 
$\begin{matrix}O\\ \backslash\!\backslash\\ C-CH_2\\ / \quad \backslash \\ M \qquad M\end{matrix}$. This could be reduced either to a metal acyl species $M-(CO)-CH_3$, or to a bridged alkyl species 
$\begin{matrix}H_2C-CH_2\\ / \quad \backslash \\ M \qquad M\end{matrix}$. Addition of hydrogen to the former species could entail propagation. Addition of hydrogen to the latter species could either result in termination under production of ethane, or yield ethyl–hydrido species participating in the propagation step.

To summarize, the current knowledge of organometallic chemistry and homogeneous catalysis provides evidence that CO insertion into a metal–alkyl bond is feasible, whereas its insertion into a metal–hydrogen bond appears to be dubious. Furthermore, it has been indicated—though not unambiguously proved—that F–T synthesis can occur in homogeneous systems, provided that suitable activation of CO is achieved. These topics are currently being studied.

5. THE REVIVAL OF THE CARBIDE THEORY

(*a*) *Dissociative adsorption of CO*

Ford's (1970) survey article, which summarized the relevant thermodesorption, isotopic, infrared, and further studies, presented the adsorption of CO as a unique example of non-dissociative adsorption of a biatomic molecule on a metal surface, in line with the then prevailing interpretation. The high dissociation energy of 1.06 kJ/mole was considered to make disintegration of the CO molecule possible only under its extraordinary activation, as is, for example, the high temperature and electrostatic field in field emission microscopy, or the energy of an impacting electron beam. However, the possibility of CO dissociation on some metals at mild temperatures (Baker and Rideal, 1955; Oda, 1955; Escoubes and Eyraud, 1966; Gregg and Leach, 1966) was not considered.

The CO decomposition over metals can take place either through disproportionation (Boudouard reaction)

$$2CO = C_s + (CO_2)_g,$$

or through its dissociation into chemisorbed carbon and oxygen

$$(CO)_s \rightleftharpoons C_s + O_s.$$

A further possibility involves the participation of hydrogen:

$$(CO)_s + H_2 \rightarrow C_s + (H_2O)_g.$$

In the beginning of the seventies, increasing evidence of dissociative chemisorption of CO at relatively low temperatures became available (Bickley *et al.*, 1971; King *et al.*, 1972; Goymour and King, 1973; Madden and Ertl, 1973). Direct proof was eventually given by UV and X-ray photoelectron spectra (UPS, XPS). UPS in the CO/W(100) system indicated (Baker and Eastman, 1973) that CO in its adsorption β-state is strongly perturbed; these results were compatible with the dissociative mode of CO adsorption. Shortly thereafter, a series of UPS and XPS studies have provided convincing evidence that the dissociation of CO occurs on W (Eastman *et al.*, 1974), Mo (Atkinson *et al.*, 1974), Fe (Kishi and Roberts, 1975), and other metals (Joyner, 1977a) at room temperature, while on Ni (Joyner and Roberts, 1974) and Co (Moyes and Roberts, 1977) only at higher temperatures. These and numerous further studies (*see* Joyner, 1977a) have shown that dissociation of CO requires a different temperature on different metals. At present, it is firmly established that at the temperature of CO hydrogenation to hydrocarbons, the adsorbed CO reacts—though not at a high rate—to form CO_2 and surface carbon C_s (Dwyer and Somorjai, 1978; Matsumoto and Bennett, 1978; Low and Bell, 1979; McCarty and Wise, 1979; Krebs and Bonzel, 1980; Kelley and Goodman, 1982; and many others). However, the detailed mechanism is still open to discussions. Direct unassisted dissociation is preferred by most authors, but the disproportionation reaction must also be taken into consideration.

This change in the view on the CO interaction with metals necessitated a profound effect on mechanistic concepts of CO hydrogenation. New consideration was given to the earlier results of Craxford and other authors pointing to the high rate of hydrogenation of deposited carbon and suggesting this carbon as the primary intermediate in the synthesis of hydrocarbons.

(*b*) *New evidence for the formation and reactivity of C_s*

Wentrcek *et al.*'s (1976) report at the end of 1975 revived the basic idea of the then generally abandoned carbide theory, namely that formation of the adsorbed carbon initiates hydrocarbon synthesis from CO and H_2. The authors observed that carbon freshly deposited on a Ni/Al_2O_3 catalyst by disproportionation of CO can be quantitatively hydrogenated into methane at 550 K and 3.5 atm (350 kPa) at the same or even higher rate compared to the methane production from mixtures of CO and H_2 under identical conditions. Peaks in Auger electron spectra pointed to a carbide-like surface species, different from the less active stable bulk carbide. By heating to 720 K, the active carbon was converted into a non-reactive species, probably graphitic in nature.

Shortly thereafter, Araki and Ponec (1976) presented results of methanation studies on nickel films at 520 K and below 100 Pa. They showed that hydrogenation of the carbon freshly formed on the surface by disproportionation of CO was much faster than the steady-state hydrogenation of CO into methane at the same temperature and hydrogen pressure. Further, using ^{13}CO to deposit carbon, and admitting thereafter a mixture of ^{12}CO and H_2, at the beginning they obtained mainly $^{13}CH_4$; the ratio of $^{13}CH_4$ formation was equal to the rate of hydrogenation of freshly formed carbon.

Finally, almost at the same time, Jones and McNicol (1977) submitted a paper declaring dissociation of CO as a prerequisite for the hydrocarbon synthesis from CO and H_2. Their arguments were based on some well-known similarity of the F–T synthesis and the Haber synthesis of ammonia from N_2 and H_2. The authors extended this analogy to the mechanistic schemes. In the Haber process, adsorbed nitrogen dissociates into atoms, which are probably hydrogenated stepwise into imino- and amino-radicals, and eventually into NH_3. Hence, Jones and McNicol proposed that CO hydrogenation might start by the dissociation of $(CO)_s$ and formation of C_s, and proceed by its consecutive hydrogenation to $(CH)_s$, $(CH_2)_s$ and $(CH_3)_s$ intermediates. Besides methane, higher hydrocarbons can also arise from these intermediates through successive addition or insertion reactions. The primarily formed active carbon was stated to differ from the less reactive bulk carbide.

These three pioneering papers were immediately succeeded by an avalanche of studies dealing with the mechanism of methanation and F–T reaction. There has been wide application of modern techniques, particularly of surface sensitive spectroscopies. The main points of these mechanistic investigations will be outlined below.

(*c*) *Formation and properties of the deposited carbon*

As already mentioned, it has not been clarified which mechanism of C_s formation predominates under the conditions of CO hydrogenation. In numerous early studies, a much higher rate of CO hydrogenation compared to CO disproportionation was reported (Section 3(b), 3(c)). This has been confirmed in recent experiments with promoted iron (Matsumoto and Bennett, 1978), while diverse results have been obtained with nickel. With Ni at 443 K and CO pressure of 50 kPa, Biloen *et al.* (1979) found that the rate of CO disproportionation was lower than the rate of its hydrogenation. Goodman and White (1979), Goodman *et al.* (1980a) and Kelley and Goodman (1982) claimed at 453 K and $P_{CO} = 3$ kPa approximately the same rates of CO disproportionation and hydrogenation, and of C_s hydrogenation. Finally, Araki and Ponec (1976), working at 523 K and $P_{CO} = 64$ Pa, reported rates of CO disproportionation an order of magnitude higher than for CO hydrogenation. It is likely that pressure and/or temperature have a great effect on the relative rates of CO hydrogenation and disproportionation. Currently, the dissociation $(CO)_s \rightarrow C_s + O_s$ is commonly taken as the first step which is succeeded by the hydrogenation both of C_s and O_s. In such a mechanism, hydrogen could account for the observed appreciable acceleration in the formation of C_s, provided the surface oxygen O_s is removed from the surface more effectively by reaction with hydrogen than with CO, which entails a much higher steady-rate coverage of O_s in the latter case. In general, however, there is but little or no observed coverage by O_s.

Recently, the idea of direct simultaneous formation of C_s and $(H_2O)_s$ by the reaction $(CO)_s + yH_s \rightarrow C_s + (H_yO)_s$; $y = 1, 2$, has been revived (Ho and Harriott, 1980; Wang *et al.*, 1981). Ho and Harriott have introduced the idea of only one site necessary for hydrogen adsorption and dissociation. This bears some resemblance to the early proposal of Craxford (1939) that some surface reactions may run according to the scheme $R_s + (H_2)_g + S \rightarrow (RH)_s + H_s$ (S denotes free site). In the modern atomistic terminology of Masters (1979), hydrogen is heterolytically split into metal-bonded anion and reactive proton, which attacks the adsorbed alkyl or CO.

In any event, C_s freshly deposited by CO disproportionation can be readily hydrogenated. The rate is often comparable to that of CO hydrogenation or is even higher, but in many cases almost exclusively methane results (Dwyer and Somorjai, 1978; Matsumoto and Bennett, 1978; Rabo *et al.*, 1978; Goodman and White, 1979;

Kelley and Goodman, 1982; and many others). However, the deposited carbon undergoes hydrogenation at such low temperatures that $(CO)_s$ still does not dissociate and does not react with hydrogen (Rabo *et al.*, 1978; Low and Bell, 1979; McCarty and Wise, 1979). Thus, C_s *can* act as precursor to hydrocarbons produced by hydrogenation of CO, but under some conditions still other mechanisms which do not involve C_s can operate or even predominate. Of great interest, therefore, are experiments in which a surface precovered with $^{13}C_s$ by disproportionation of ^{13}CO was exposed to the gaseous mixture of H_2 and ^{12}CO. In this way, Araki and Ponec (1976) found on Ni that most of the initially formed methane originated from C_s. But in similar experiments by Biloen *et al.* (1979) and Wentrcek *et al.* (1976), the competition of $(CO)_s$ with C_s in the formation of methane was appreciable from the start of the experiment. It appears as likely that the result of Araki and Ponec can be accounted for by high coverage of C_s, close to a monolayer. The initial rate of $^{13}CH_4$ formation was about the same as that of C_s hydrogenation. Under steady-state conditions of CO hydrogenation the coverage of Ni by C_s is but moderate (Goodman *et al.*, 1980a, b; Happel *et al.*, 1980; Kelley and Goodman, 1982), and thus successful competition between preadsorbed C_s and fresh C_s from CO is possible. On cobalt precovered with almost a monolayer of $^{13}C_s$ (similar to the steady state with this metal), the rates of methane formation from C_s and CO were comparable to each other from the beginning (Sachtler *et al.*, 1979). On ruthenium, the steady-state coverage of C_s is again but low (Goodman and White, 1979; Kelley and Goodman, 1982). When, however, Ru was richly precovered with $^{13}C_s$, the production of methane from CO was dominant from the beginning (Sachtler *et al.*, 1979). Finally on iron catalyst, the deposited C_s did not participate significantly in the hydrocarbon synthesis (Matsumoto and Bennett, 1978). This may be due either to the inherent lower activity of C_s formed by CO disproportionation in this case, or to its gradual deactivation (Sachtler *et al.*, 1979). Such a loss of activity of C_s for hydrogenation, without a change in its carbidic nature, has been found (McCarty and Wise, 1979; Bonzel and Krebs, 1980; Krebs and Bonzel, 1980). This problem might be elucidated by means of monitoring the methane production after CO has been eliminated from the $CO + H_2$ feed in the steady state. However, first an enhanced rate of methane production was observed (Matsumoto and Bennett, 1978; Ekerdt and Bell, 1979; Ho and Harriott, 1980), up to 100 times higher than in the steady state. Moreover, the most rapidly hydrogenated adspecies need not be carbon; $(CH)_s$, or possibly even $(CH_2)_s$, appears to be, besides C_s (Happel *et al.*, 1980), the dominating carbonaceous adspecies at the steady state (Matsumoto and Bennett, 1978; Ekerdt and Bell, 1979; Bonzel and Krebs, 1980; Goodman *et al.*, 1980b). The increase in the methanation rate after CO has been switched off is probably due to the removal of the inhibiting effect of CO (Matsumoto and Bennett, 1978; Ho and Harriott, 1980). This invalidates somewhat the argumentation that CO hydrogenation runs through C_s, based upon the equal rates of hydrogenation of C_s and CO.

As already mentioned, the activity of the freshly formed C_s gradually decreases. Either transformation of C_s into a less active state, or its removal from the surface can be responsible for that effect. Under the conditions of F–T synthesis, diffusion of surface carbon into the bulk under formation of carbide does not occur with Ru, and is only of minor importance with Ni and Co. With Fe catalysts, however, a full-scale hydrocarbon synthesis with steady-state activity and selectivity takes place only after the catalyst has been carburized into a considerable depth. Niemantsverdriet and van der Kraan (1982) have shown that all the findings are compatible with a competition model: $(CO)_s$ dissociates on Fe atoms at the catalyst surface, and the C_s

formed either is consumed by the carbidation reaction, or it reacts with xH_s to give $(CH_x)_s$ species, or it is deactivated by interaction with other C_s species. Initially, C_s is mostly spent by the carbidation process. Only after the bulk of the catalyst becomes carbided, progressively more C_s is available for hydrocarbon synthesis. The difference between Fe and the other F–T catalysts can be understood in terms of the different rates of carbon diffusion into the bulk.

Inevitably connected with CO hydrogenation is the gradual formation of inactive carbon, which blocks the active surface sites and slows down the production of hydrocarbons. In fact, there are more forms of 'inactive' or 'free' carbon. They range from the relatively harmless filaments (whiskers) of amorphous carbon which leaves a large portion of the surface free and allows fairly easy regeneration of the catalyst activity by hydrogenation at moderately elevated temperatures (Storch *et al.*, 1951; Ekerdt and Bell, 1979; McCarty and Wise, 1979) up to the compact and tenacious, graphite-structured layers which effectively inhibit CO hydrogenation and are removable only by oxidation. Problems of minimizing the surface carbon deactivation have been studied extensively.

(*d*) *Hydrogenated intermediates and their role in the chain growth*

The return of the carbidic theory has also revived the idea of stepwise hydrogenation of the surface carbon formed C_s to $(CH_x)_s$ intermediates ($x = 1$–3) (e.g., Jones and McNicol, 1977; Joyner, 1977b; Matsumoto and Bennett, 1978).

Direct proof of the occurrence of $(CH_x)_s$ intermediates is difficult, since their surface concentration may be very low. Thus, Happel *et al.* (1980) concluded from kinetic measurements on the catalyst Ni/SiO_2 that the coverage of the surface with C_s and $(CH_x)_s$ species amounted to 20% and less than 4%, respectively. Spectroscopic methods (IR, XPS, EELS) would seem to afford the most direct evidence, provided they can be made sufficiently sensitive. These methods are, however, hardly applicable under the actual reaction conditions, and this may give rise to artefacts, as interactions of the $(CH_x)_s$ species between themselves and with H_s may take place. This can even cause some escape of H_2 or CH_4 before spectroscopic measurements are performed, and thus shift the distribution of intermediates to the hydrogen-deficient species, including C_s. Furthermore, the assignment of the infrared bands may be controversial (cf. Blyholder and Neff, 1962, vs. Dalla Betta and Shelef, 1977). Thus, infrared spectra have provided no clear-cut evidence of various $(CH_x)_s$ species on the reacting catalyst surface (Ekerdt and Bell, 1979; King, 1980). Bonzel and Krebs (1980) interpreted their XPS data on Fe(110) surface exposed to CO with a great excess of H_2 in terms of a mixture of $(CH_x)_s$ species, with the $(CH)_s$ species perhaps prevailing. The EELS results on Ni(111) surface pointed to $(CH_x)_s$ species, probably $(CH)_s$ species, but the experimental conditions differed radically from those existing in F–T and methanation reactions (Bertolini and Imelik, 1979).

The chemical approach to the problem uses 'scavengers', i.e., unsaturated compounds able to capture reactive surface species in the course of CO hydrogenation. The most complete study has been reported on Ru by Baker and Bell (1982) (for previous work *see* references therein). By adding small amounts of benzene or alkenes, the authors have proved the presence of $=CH_2$ and $-CH_3$ groups on the surface, together with slight amounts of higher alkyls. The results, however, are only qualitative and do not provide actual surface concentrations, since reactivity of the particular species is not known. The detected carbene $=CH_2$ may to a large extent arise from $(CH)_s$ or possibly from $(CH_3)_s$.

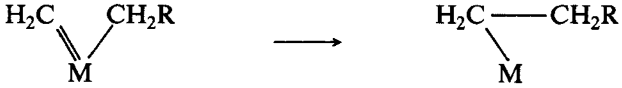
A different problem is presented by the question of whether some of the $(CH_x)_s$ species actually participate in chain growth at all, and if so, which species and through what mechanism. The original hypothesis of Fischer and Tropsch (1926a) that $(CH_2)_s$ species are the chain-building units lacked convincing experimental support for a long time. On the contrary, a serious argument against this idea has appeared in the fact that the removal of CO from the reaction mixture leads immediately to a radical decrease in the production of hydrocarbons other than methane. This decrease cannot be accounted for by an increased concentration of surface hydrogen only (Storch *et al.*, 1951; van Barneveld and Ponec, 1978; Matsumoto and Bennett, 1978; Ekerdt and Bell, 1979; Low and Bell, 1979). A possible explanation may be a very limited linking ability of $(CH_x)_s$ units compared to the rate of the chain growth by incorporation of CO groups.

On the other hand, Rabo *et al.* (1978) found appreciable (though lowered) formation of C_2 and higher hydrocarbons even after the CO feed had been stopped, particularly at low temperatures. Furthermore, Biloen *et al.* (1979) observed multiple incorporation of $^{13}C_s$ predeposited on Ni into higher hydrocarbons. The probability of incorporation of the ^{13}C and ^{12}C units into the hydrocarbons was roughly determined by the relative coverage of the surface with $^{13}C_s$ and $^{12}C_s$, respectively. This points to the participation of sufficiently 'active' $(CH_x)_s$ species in the chain build-up rather than to the insertion of CO group. Bonzel *et al.* (1980) concluded from experiments on Fe that both the $(CH_x)_s$ polymerization and the $(CO)_s$ insertion could be operative in chain growth.

Experiments of another type have been based on the decomposition of molecules containing CO and/or CH_2 groups on F–T catalysts in the presence of hydrogen. Work with the 1:1 mixture of ketene and hydrogen over Co catalyst (Warner *et al.*, 1946) yielded results suggesting that the hydrocarbons formed were built mainly from the CH_2 part of the ketene molecule, while its CO part participated marginally if at all. Blyholder and Emmett (1959, 1960) performed experiments with addition of radioactively labelled ketene to the synthesis gas fed to the catalysts Fe and Co. The results were at first evaluated as indicative of participation of the CO groups from the split ketene molecule in the chain propagation. Only at a later reconsideration was it recognized that the $(CH_2)_s$ species from the decomposed ketene contributed significantly to the chain build-up (*see* Ponec and van Barneveld, 1979; Biloen and Sachtler, 1981; Ponec, 1983). Break-up of CH_2Cl_2 in hydrogen was reported to furnish $(CH_2)_s$ species which can polymerize (Ponec and van Barneveld, 1979). The most convincing proof that $(CH_x)_s$ species are readily incorporated into growing hydrocarbon chains has been provided by Brady and Pettit (1980, 1981) who worked with mixtures of CH_2N_2 and hydrogen over various transition metals. Hydrocarbons of a distribution very similar to that found in F–T synthesis were obtained. The presence of hydrogen is necessary to initiate the chain build-up by formation of $(CH_3)_s$ units.

The apparent contradiction of the evidence for and against the incorporation of $(CH_x)_s$ units into the growing chain can be reconciled by assuming that only active and energy-rich $(CH_2)_s$ species can insert into the alkyl-to-surface bond. Such are the $(CH_2)_s$ species freshly formed by hydrogenation of $(CO)_s$ or C_s, or by dissociation of diazomethane, dichloromethane or ketene. The available results, however, do not allow us to claim that chain growth can proceed exclusively by one definite mechanism. Both the $(CO)_s$ and $(CH_2)_s$ insertion mechanism can participate in the chain build-up. According to the particular catalyst and reaction conditions, one of the mechanisms can become dominant.

Chain growth can be formulated in terms of molecular interpretation as the insertion of the surface carbene species $M = CH_2$ into an alkyl group bonded to the same metal atom (Biloen *et al.*, 1979; Biloen and Sachtler, 1981):



Analogous catalytic formation of the C–C bond from groups attached to the same metal atom occurs in the coordinative polymerization of alkenes by the Ziegler–Natta mechanism, in metathesis of alkenes, and in dehydrocyclization of cycloalkenes. The importance of the heterogeneously catalyzed interactions of π- and δ-ligands on the same metal atom was earlier pointed out by Schulz (1977) and exemplified on the hydrogenation and polymerization of alkenes.

Karzhavin's suggestion (1947) that hydrocarbon surface species may be linked together by means of $(CO)_s$ should not be ignored. Indeed, Gibson and Clarke (1961) in their experiments with equimolar mixture of hydrogen and ethylene on Co catalysts observed that addition of CO triggered dissociation of ethylene into C_1 units and synthesis of higher hydrocarbons at the cost of ethylene hydrogenation into ethane. Moreover, when ^{14}CO was used, accumulation of radioactivity in the central carbon atoms of the hexenes and heptenes produced was found. Evidently, this can be interpreted in terms of linking two hydrocarbon fragments mediated by $(CO)_s$. Most of the hydrocarbon products, however, were formed without involvement of CO, and this indicates that only ethylene and/or $(CH_2)_s$ species participated in the build-up of their chains. This interpretation of course differs radically from that one offered by the authors themselves in terms of oxygenated C_1 intermediates.

An excellent review and deep analysis of the problems of chain growth has recently been presented by Biloen and Sachtler (1981), who consider the insertion of $(CH_2)_s$ units into a surface bonded alkyl as the most likely chain growth process. This is also our view, with the reservation, that under usual conditions of F–T synthesis, CO plays an active role in the formation of active $(CH_2)_s$ species able to lengthen the surface alkyl chain.

(*e*) *Nature of the active centre in hydrocarbon synthesis*

Structures ranging from a single metal atom to a large ensemble of atoms have been proposed for surface centres active in the synthesis of hydrocarbons from CO and H_2. Suggestions of one- and two-atomic centres have been mentioned in Section 4(bi). Evidence in support of the ensemble nature of the reaction centres has been provided firstly by work with binary alloys. If some step in the hydrogenation of CO requires more than one surface site and the active metal on the surface is diluted in a random fashion by an inactive component, the decrease in activity has to be stronger than linear in the surface concentration of the active metal. The effect is most pronounced with low surface concentrations of the active component, implying a high proportion of inactive single sites.

This idea was first applied to CO hydrogenation by Araki and Ponec (1976). They worked with Ni–Cu alloys, which exhibit only 10 ± 5 at.% of Ni on the surface for a wide range of bulk compositions (Ponec, 1980). Copper bonds CO but weakly in 'on-top' positions and is inactive in its hydrogenation. Moreover, the electronic structure of Ni atoms and their chemisorption properties towards CO are only little changed in their alloying with Cu (Ponec, 1979). Hence the geometric effect of alloying here predominates. The activity of the Ni–Cu alloys in CO hydrogenation was drastically lower compared to pure Ni (van Barneveld and Ponec, 1978). Since the rate constants and hence the apparent activation energies changed only slightly, the decrease in activity could be due mainly to the pre-exponential term in Arrhenius equation. Araki and Ponec (1976) ascribed this effect to the dissociation of CO occurring in a 'valley' formed by an ensemble of Ni atoms. There have been different estimates of the number of atoms in such an ensemble. A large ensemble has been mentioned by Ponec (1983). Infrared spectra, thermal desorption and other techniques have provided additional evidence of CO dissociation on multiply coordinated sites, which have been suggested to consist of two to four Ni atoms (Gałuszka *et al.*, 1981). The data of Araki and Ponec (1976) and of van Barneveld and Ponec (1978) appear to be actually compatible with only two sites in a reaction centre: in the alloys studied with the surface concentration of Ni atoms amounting to 0.1, the requirement of two neighbouring sites in the case of their random distribution should reduce the activity roughly to $(0.1)^2 = 0.01$. This was actually observed.

The ensemble effect in the hydrogenation of CO was also found by Bond and Turnham (1976) on Ru–Cu alloys. The authors concluded that up to four to five Ru atoms participated in the reaction centre, and that it was the hydrogenation of a central carbonaceous species by the surrounding adsorbed hydrogen atoms which occurred in this centre. Luyten *et al.* (1978) reported a much less pronounced decrease in the rate of CO hydrogenation on silica-supported Ni–Cu and Ru–Cu alloys. Only the pre-exponential factor of the Arrhenius plot was diminishing as the Cu content increased, pointing again to a geometrical effect.

Clearly, it need not be only dissociation of CO which needs a multisite centre. Hydrogenation steps and possibly chain propagation steps may, and very likely do, require at least one extra site for the reacting hydrogen, adjacent to the carbonaceous species.

Inhibition by H_2S is sometimes taken as evidence of the ensemble effect in CO dissociation. However, the primary factor in this inhibiting effect may be rather the competition between H_2S and the multiply bonded CO for the same adsorption sites (Kishi and Roberts, 1975; Jones and McNicol, 1977; Joyner, 1977b; Rewick and Wise, 1978; and many others). Hence, the stoppage of the hydrogenation of CO after its exclusion from the multicoordinated adsorption sites suggests that hydrogenation reactions can start only with multiply bonded CO molecules. Dissociative adsorption of CO on Ni is very strong and does not allow the multicoordinated adsorption of CO to take place, though the simple on-top adsorption of CO may even be enhanced (van Dijk *et al.*, 1976; Rewick and Wise, 1978). Agrawal *et al.* (1981) and Fitzharris *et al.* (1982) recently interpreted their results on Co and Ni, respectively, in terms of geometric blocking of sites for CO dissociation by adsorbed sulphur; the rate-determining step of the reaction needed two sites.

Some authors (Erley and Wagner, 1978; Rostrup-Nielsen and Pedersen, 1979; Goodman and Kiskinova, 1981), on the contrary, have claimed that one S atom deactivates four to ten sites on Ni. This points to an electronic rather than geometric mechanism of the blockage. An explanation can be provided in terms of Blyholder's well-known model of the back-donation mechanism of CO chemisorption on metals. If the negative charge of the metal is lowered by the strong electron-withdrawing action of sulphur on a neighbouring site, the CO–metal bond is weakened relative to the C–O bond, and dissociation of CO is impeded. Electron donors such as alkali act in the reverse direction and give rise to an enhanced CO dissociation. A similar picture follows from the model accounting for the adsorption of gases on transition metals in terms of an interplay of free and localized electrons (Knor, 1981): sulphur blocks the localized portion of d-electrons in the metal, and thereby the localized interaction of the CO molecule with the surface is weakened and its dissociation inhibited. This interpretation of the effect of sulphur on the metal d-electrons is consistent with the UPS results in the S/Ni(100) system (Nguyen *et al.*, 1979).

(*f*) *Question of a common initiation step in methanation and F–T reaction*

Arguments presented in the preceding sections show that formation of C_s is the initiation step in hydrocarbon synthesis from CO and H_2. One may ask whether this step is identical in methanation and F–T reaction.

Craxford and Rideal (1939) and Fischer and Pichler (1939) presumed that the concentration of surface carbon decides whether methane or higher hydrocarbons are formed. The content of methane in the synthesized products increases with the H_2/CO ratio and temperature. This indicates that hydrogenation of some $(CH_x)_s$ species to methane and formation of C–C bonds are competing processes, and that at least two slow steps with different activation energies are operative. Such a situation may occur at a point of bifurcation in the reaction pathway. Increased selectivity of the methane formation with temperature could be accounted for by a lower activation energy for the C–C bond formation compared with the hydrogenation to methane. As an alternative, one can suggest that the formation of C_s from $(CO)_s$ has a lower activation energy than the hydrogenation of C_s to $(CH)_s$, and that the subsequent hydrogenation steps are relatively fast. In such a case, the steady-state coverages of C_s and $(CH)_s$ could strongly decrease as temperature increases, and hence the formation of C–C bonds would decline for purely geometrical reasons.

Evidence suggesting that C_s may be a common intermediate both for methane and higher hydrocarbons has been inferred by van Barneveld and Ponec (1978) from experiments on Ni–Cu surfaces rich in copper. The observed drop in the methanation activity compared with pure Ni surfaces was much higher than the decrease in the production of C_2 and C_3 hydrocarbons. In conjunction with the presumed ensemble effect in the dissociation of CO, this result points to C_s as a common intermediate. On the other hand, the relatively enhanced yield of C_2 and C_3 products on alloys with a high Cu content is somewhat puzzling.

Biloen *et al.* (1979) precovered Ni/SiO_2 catalyst with $^{13}C_s$, and then fed to it a mixture of ^{12}CO and H_2. The approximately uniform distribution of ^{13}C in the hydrocarbons produced up to C_4 suggests that methane and higher hydrocarbons are formed from the same building blocks, namely from the $(CH_x)_s$ species. Qualitatively the same conclusion can be drawn from the work of Rabo *et al.* (1978) on Ni, Co and Cu. Some $(CH_x)_s$ species also seem to be common for the build-up both of methane and of higher hydrocarbons on Fe catalysts (Matsumoto and Bennett, 1978). Further studies corroborate this view and relate oxygenated intermediates in the CO hydrogenation solely to the formation of oxygenated products (Joyner, 1977a; Ekerdt and Bell, 1979; Low and Bell, 1979).

(*g*) *Relative activity of metals in methanation and F–T synthesis*

Vannice (1976, 1977) attempted to correlate the methanation activity of metals with the then available initial heats of CO adsorption. However, the assumption of a non-dissociative adsorption of CO in all cases was implied.

If active surface carbon is the first intermediate in methanation and F–T synthesis, then only metals which readily dissociate CO can be good catalysts for these reactions (Jones and McNicol, 1977; Joyner, 1977b). However, W and Mo dissociate CO below 170 K, but their methanation activity is poor. Therefore, an additional condition was proposed: the carbon–metal bond must not be so strong that the hydrogenation of C_s is difficult (Joyner, 1977b) (the finding of Kelley *et al.*, 1977, that very clean W is a good methanation catalyst is, however, not in line with this condition). Reducing carbon–metal bond strength by addition of electron withdrawing promoters was suggested to facilitate the hydrogenation of C_s on the metals in question (Joyner, 1977b).

Ponec and van Barneveld (1979) have documented the proposals mentioned by using the metal–carbon and metal–oxygen dissociation energies in biatomic carbides and oxides. Their sum was close to the dissociation energy of CO on the metals catalyzing methanation and F–T synthesis, thereby indicating the thermodynamic possibility of CO dissociation. One can add, however, that this argument in favour of the formation of C_s is valid only under the assumption that C_s is formed exclusively by dissociation of CO. The thermodynamic requirement of exothermicity becomes less stringent if hydrogen is involved in the formation of C_s.

On the other hand, metals which chemisorb CO non-dissociatively (Pd, Pt, Ir) activate the C–O bond for hydrogenation and at higher pressures are good catalysts for the synthesis of alcohols (Rabo *et al.*, 1978; Ponec and van Barneveld, 1979).

Brodén *et al.* (1976) proposed characterizing the activation of the CO molecule by weakening the carbon–oxygen bond displayed through the energetic gap between the 1π and 4δ emission peaks in UPS spectra. This gap ranges from 2.6 to 3.5 eV for various metals. Metals with the gap between 3.1 and 3.5 eV rank among those best suited for F–T catalysis. Metals with this gap exceeding 3.5 eV dissociate CO even at low temperatures and bind C and O too firmly. However, the relationship of this criterion to the probability of CO dissociation has been questioned by Bonzel and Krebs (1982). The authors have brought further support to the analysis by Benziger (1980) who considered the adsorption energy of the C and O species formed from CO as a thermodynamic driving force, on which basis the relative rates of CO dissociation on different metals can be understood.

(*h*) *Kinetic studies*

Under typical conditions, hydrocarbon synthesis is sufficiently slow as to be governed by surface processes only, and diffusion is not a limiting factor. Hence, correlations of the reaction rate with the applied partial pressures of H_2 and CO can provide some useful information in the discussions on the reaction pathway. Such correlations have been established mostly for the rates of methanation only, and are of two principal kinds:

1. The 'chemical engineering' power expression

$$N = k_0 \exp(-E/RT)\, P_{H2}^{m}\, P_{CO}^{n}$$

2. Some simplified form based on the Langmuir kinetic treatment of an adsorption–desorption process, such as

$$N = \frac{kP_{H2}^{x}\, P_{CO}^{y}}{(1 + K_1P_{CO} + K_2P_{H2})^{z}},$$

where k and K_i may be temperature dependent.

The fit of the correlations is, however, often rather poor, with relative deviations of 10 to 15%. This is partly due to the low reproducibility of the experiments. An important point is to measure kinetic data under differential conditions, and to establish the degree of dispersion of the catalyst (Vannice, 1975, 1976, 1977). This permits a sensible comparison to be made in terms of specific activities, i.e., on the turnover basis (turnover number is given by the number of molecules formed or reacted per second on one metal site).

Empirical power correlations have been summarized up to 1976 by Vannice (1976). They are valid only for the particular conditions at which they have been measured (Polizzotti and Schwarz, 1982). For the modelling of the methanation mechanism they are of a very limited significance.

Only methanation kinetics have been treated on Ni catalysts by the correlations of the Langmuir type (e.g., Huang and Richardson, 1978; Harriott and Ho, 1981; Wang *et al.*, 1981). All the results obtained reflect the fact that, in the low pressure region of CO, methanation rate increases with P_{CO}; at medium CO pressures, it is but slightly dependent on P_{CO}; and at high CO pressures it is inhibited. Together with the finding of a low steady-state coverage of C_s on the working Ni surface (cf. Section 5(c)) while that of $(CO)_s$ is rather high, the kinetic results indicate that the rate-determining step involves adsorbed H_s species competing for adsorption sites with $(CO)_s$, and that C_s is removed from the surface by hydrogenation with a rate constant higher than that for the formation of C_s from $(CO)_s$, but of the same order of magnitude. Hence, disproportionation of CO on Ni is not rate-limiting. Neither can some step in the hydrogenation of C_s be the only rate-limiting process, as was earlier hypothesized.

Studies on Fe catalysts in the pressure range of 10 to 20 bar (1 to 2 MPa) (Dry *et al.*, 1972) and at 1 bar (100 kPa) (Krebs *et al.*, 1979) again show that the activity in CO hydrogenation increases with the pressure of hydrogen, so that dissociation of $(CO)_s$ cannot be rate-determining. The negative dependence on CO pressure when the total pressure is atmospheric suggests competition for surface sites between H_s and $(CO)_s$. The slowest step appears to be hydrogenation of some $(CH_x)_s$ species. This is corroborated by the high C_s coverage on the working Fe surface (Matsumoto and Bennett, 1978; Krebs *et al.*, 1979).

On Ru catalysts, the power correlations indicate that the methanation rate at low CO pressures is proportional to P_{CO} (Vannice, 1976). The inhibiting effect of CO begins to prevail at the increasing P_{CO}, until it ceases at high pressures, as with Fe. By contrast to other catalysts, Ru shows a stronger than linear dependence of the activity on P_{H_2}. This makes Ru catalysts the only system in which any significant operation of the initial reaction $(CO)_s + 2H_s \rightarrow C_s + H_2O$ appears to be excluded. The working surface of Ru is almost completely covered with $(CO)_s$ (Cant and Bell, 1982), but with little C_s (Goodman and White, 1979). The somewhat puzzling suggestion of carbon multilayers on the working surface of Ru (Ekerdt and Bell, 1979) may be accounted for by moderately active filaments of carbon, as with Fe catalysts (Dwyer and Somorjai, 1978). While on Ni catalysts with low C_s coverage the production of C_{2+} hydrocarbons is low, Ru catalysts can form a broad spectrum of hydrocarbons, similar to Fe and Co catalysts at high coverage of C_s. Thus, with Ru the concept of a C_s intermediate in the sense of the carbidic theory is the least founded of all the active metals. The idea of Rabo *et al.* (1978) of two parallel reaction pathways involving hydrogenation of dissociated and undissociated carbon monoxide, respectively, is best acceptable just with Ru. This has been supported recently by Cant and Bell (1982).

The studies of the overall kinetics have not thus far provided an unambiguous confirmation of any of the proposed mechanistic schemes, since several models are consistent with the kinetic data. Nevertheless, the studies have been helpful in disproving some of the potential reaction routes. Biloen and Sachtler's (1981) view is here relevant; they consider that the existence of the carbidic overlayer and its variation with the partial pressure of reactants can no longer be ignored when discussing the reaction kinetics or comparing the activities of various metals.

Mention should be made of the pulse-technique analysis of the kinetics of the F–T reaction by Dautzenberg *et al.* (1977). The specific activities for methanation obtained by Vannice (1975, 1976, 1977) are several orders of magnitude lower than those for other reactions. This might be due either to the low number of active sites on the surface, or to their low intrinsic activity. Dautzenberg *et al.* (1977) fed pulses of $CO+H_2$ to the catalyst Ru/Al_2O_3 and observed that the product distribution narrowed as the time of the pulse decreased and was approaching the one predicted by the Flory–Schulz polymerization model. An additional assumption was made that steady-state concentrations are achieved quickly both by the C_1 species which initiate the hydrocarbon synthesis and by the C_1 species which are attached to the growing hydrocarbon chains. The authors concluded that the low activity of the Ru/Al_2O_3 catalyst in the F–T reaction is not due to a low number of surface sites, but to the low intrinsic activity of the Ru atoms. The growth rate was estimated to be about one $-CH_2-$ group per minute for each growing intermediate. Therefore, it is the propagation activity and not the rate of initiation that limits the F–T reaction on the catalyst studied.

6. THEORETICAL STUDIES OF CARBON MONOXIDE HYDROGENATION

Attempts have been made to apply theoretical methods to elucidate some points in the mechanism of catalytic hydrogenation of CO. Leaving aside the numerous papers dealing with chemisorption of pure CO and H_2, we will mention only the few published studies of their interaction.

The *ab initio* generalized valence bond method (Goddard *et al.*, 1977) provided the bond energies and geometries of the presumed intermediates in methanation on nickel. The surface was represented by one or two Ni atoms. The results were used to assess the reaction mechanism. The authors concluded that with chemisorbed formyl radicals Ni–CHO present on the surface one obtains a series of exothermic steps constituting a chain reaction for producing methane while regenerating the formyl radical. Dissociative chemisorption of CO at higher temperatures leads to C_2 surface species that may be catalytically active.

Kölbel and Tillmetz (1974) used the Extended Hückel Theory followed by Mulliken population analysis to compute the binding energies and electronic structures of surface complexes formed from $CO+H_2$ mixtures with single Fe, Co and Ni atoms. The results suggested that enol complexes of the Anderson type attached to Fe and Co atoms are stable, whereas a methylene type complex is formed with Ni. In another paper (Kölbel and Tillmetz, 1972) the authors inferred from the results of the same method that the enol complex $Fe=C(OH)H$ can either be hydrogenated to give methane, or can undergo condensation with another complex to form a C_2 aldehyde.

Kasowski and Caruthers (1980) applied the extended muffin-tin orbital theory to the interaction of $CO+H_2$ on Ni(001) surface. The results were consistent with two mechanisms of methanation:

1. The CO triple bond does not break on Ni(001), but it can be broken by disproportionation of $(CO)_s$ and another chemisorbed or gas-phase CO molecule into CO_2 and C_s. The latter species can be hydrogenated to CH_4.
2. CO and H_2 form on Ni(001) surface formaldehyde whose carbon–oxygen bond can break and a $(CH_2)_s$ species can arise. This can be reduced to CH_4.

Feibelman (1981) reported a self-consistent calculation of the electronic structure of the carbidic and graphitic carbon on Ru(0001) surface for a chosen geometric model. The $2p_z$ orbital of the carbidic carbon has a peak in the density of states near the Fermi level, which perhaps represents the 'dangling bond' responsible for the chemical reactivity. By contrast, the p_z orbitals of the graphitic carbon are bonded with each other and hence are unavailable for chemical interactions.

When judging the conclusions of these theoretical studies one should bear in mind that both the models and the calculation procedures have involved debatable simplifications and assumptions, and that the interpretation has been clearly biased by the then prevailing mechanistic views on F–T synthesis.

7. CONCLUSION

The most important suggestions on the mechanism of F–T synthesis and methanation can be summarized as follows.

(*a*) *Hypotheses of initiation*

The carbidic hypothesis proposes that first an active, carbide-like surface carbon species C_s arises, and subsequently undergoes partial hydrogenation to $(CH_x)_s$ species, $x = 1, 2, 3$. In principle, the C_s species can arise in two ways:

1. Directly, i.e., by unassisted dissociation of carbon monoxide to C_s and O_s; the latter species can be removed from the surface either as CO_2 (through reaction with CO), or as H_2O (through reaction with H_2).
2. Indirectly, i.e., by reaction of the $(CO)_s$ species either with CO (disproportionation), or with H_2.

The molecule reacting with $(CO)_s$ can in principle either arrive from the gas phase (one surface site is required), or be adsorbed on an adjacent site (two sites are required for the reaction). These considerations imply that dissociation of CO is conditioned not by formation of a strong surface bond of C_s (as in bulk carbides), but rather by negative or only slightly positive free enthalpy of the reaction $CO + H_2$ or $CO + CO$, and by a low energetic barrier. The direct dissociation of CO is generally considered as most likely in the majority of cases of hydrocarbon synthesis.

The hypothesis of oxygenated intermediate suggests that the initiation step involves formation of a surface complex $(COH_x)_s$, $x = 1, 2$. This means that CO is first non-dissociatively adsorbed, and then partially hydrogenated. The complex can either yield C_s, or be hydrogenated to $(CH_x)_s$, or participate as such in chain growth; the last alternative is generally favoured.

Besides these two important alternatives, surface species formed from adsorbed alkenes, alcohols, and some other compounds can also act as chain initiators under certain conditions.

(*b*) *Hypotheses of chain propagation*

Three main mechanisms of chain propagation have been proposed:

1. Insertion of $(CH_x)_s$ species into adsorbed alkyls.
2. Insertion of a CO group into the adsorbed hydrocarbon species, followed by hydrogenation.
3. Condensation of two oxygenated adsorbed intermediates, again followed by hydrogenation.

In addition, insertion of alkenes is considered under some conditions.

(*c*) *Hypotheses of chain termination*

Originally, termination was thought to be either addition of hydrogen to the growing chain, giving rise to release of an alkane from the surface, or β-elimination of hydrogen leading to the release of an alkene. Growing evidence indicates that the main termination reaction is the release of α-alkenes, and only on their readsorption is the double bond either hydrogenated or it migrates along the chain.

Fischer's insistence upon a basic difference in the mechanisms of CO hydrogenation producing hydrocarbons and oxygenates contributed significantly (although not quite deservedly) to the disfavour of the carbide theory in the 1950s. A still more important argument against the carbide theory followed from its failure to show clearly that only sufficiently active kinds of surface carbon can participate in the synthesis of hydrocarbons. Fischer and Tropsch and some other authors guessed this when postulating a different nature of ordinary bulk carbides and the surface carbides active in the synthesis. But the methods available then were not capable of clarifying this matter conclusively.

The arguments in favour of an oxygenated intermediate were only indirect, and, as Ponec (1983) pointed out recently, some were based on an unsubstantiated interpretation of experimental results. This is particularly true for:

1. Experiments in which the radioactivity of the effluent gas was monitored when feeding a mixture of $^{12}CO + H_2$ to iron catalyst precarburized with ^{14}CO.
2. Experiments in which labelled ethanol and other oxygenates were incorporated into hydrocarbon chain.
3. Experiments with labelled ketene.

Interpretation in all these cases suffered from underestimation of the possible operation of active surface carbon and $(CH_x)_s$ species.

The rehabilitation of the carbide theory in the 1970s was preceded by experimental proofs showing that the high bond energy of the CO molecule is not prohibitive for its dissociation on metals. At first the formation of C_s was widely accepted for the initiation step in hydrocarbon synthesis. The chain growth, however, was further considered to run via an oxygenated intermediate formed by insertion of a CO group into the carbon–metal bond, as with organometallic reactions. Gradually arguments have been accumulated indicating that the linking of active $(CH_2)_s$ species is likely to be the key chain-growth mechanism (*see*, for example, Brady and Pettit, 1980, 1981).

In contrast to the typical earlier situation, the current mechanistic suggestions are characterized by admitting the possibility of simultaneous operation of different reaction routes. At bifurcation points of the reaction sequence, the kinetic probability determines which route will prevail under the given conditions.

Simultaneous occurrence of oxygenated and non-oxygenated intermediates has been involved in a number of recent studies. Kellner and Bell (1981) have proposed parallel pathways for the formation of hydrocarbons (via C_s), acetaldehyde (via CO insertion), and methanol (via hydrogenation of $(CO)_s$ in the bridge form) on supported Ru. Chain length distributions of hydrocarbons and oxygenates are similar, again pointing to a common reaction intermediate (Schulz and Zein el Deen, 1977).

The main problem of F–T synthesis is its limited selectivity. In order to overcome the Schulz–Flory distribution of products, it is desirable to understand the finer details of the mechanism of the synthesis. Our knowledge in this field is developing rapidly. However, one cannot overlook how often sophisticated up-to-date experiments ultimately lead to ideas which are very similar to those arrived at much earlier by the development of simple methods or even merely by intuition.

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