MECHANISM OF THE SYNTHESIS
OF HYDROCARBONS
FROM CARBON MONOXIDE AND
HYDROGEN

TRANSLATED BY PAUL LEVINSON: EDITED BY ERNST M. COHN
FROM THE RUSSIAN REPORT OF Y. T. EIDUS

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PREFACE

This translation of a review paper by Y. T. Eidus on the Fischer-Tropsch reaction was prepared originally for use by the Federal Bureau of Mines in connection with its research on the conversion of coal to fluid fuels. Although published in 1951, it appears to be the latest available Russian summary, written by an expert in the field and incorporating the results of a great deal of his and other Russian work up to that time.

Because of the importance of this report to a large segment of the mineral, chemical, and fuel industries of this country and because of the difficulty of obtaining and reading the original and many of the source materials, the Bureau is publishing this translation, which it believes to be of broad public interest.

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MECHANISM OF THE SYNTHESIS OF HY-DROCARBONS FROM CARBON MONOXIDE AND HYDROGEN[1]

TRANSLATED BY PAUL LEVINSON;[2] EDITED BY ERNST M. COHN[3]

FROM THE RUSSIAN OF Y. T. EIDUS[4]

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INTRODUCTION

Ten years ago we surveyed in "Uspekhi Khimii" the mechanism of the synthesis of hydrocarbons from CO and H₂ (1).[5] With new data obtained since then, mostly by Soviet researchers, our previous work (2), dealing with new forms and catalysts of the synthesis, is brought up to date by reviewing research in this field.

FORMATION OF CARBIDES

The hypothesis that carbides are intermediates in the synthesis assumes that carbon monoxide reacts with the metals of the eighth group and that this reaction is connected with the reversible reaction

$$2CO \rightleftharpoons C + CO_2 \qquad (1)$$

in a certain range of temperatures (3).

Catalysts for this reaction were considered to be the oxides of the iron group of metals (4), the metals themselves (5, 6), and the carbides of these metals.

Iron carbides were postulated to be catalysts for two reasons: Because carbide is formed when CO is passed over Fe₂O₃ at 850°[6]; and because free carbon occurs below 800° only after the carbon content in the solid phase has reached a value corresponding to Fe₃C (7).

In the presence of iron-alkali catalyst, synthol formation (8) does not go by way of carbides (9).

Some evidence was given of the formation of Fe₃C₄ (10), which decomposes into carbon and Fe₂C. Formation of Fe₂C was also noted when CO was passed over Fe₂O₃ at 275° (11). X-ray analysis of the products formed at 275° to 320° showed Fe₃C and an unknown substance, considered to be Fe₂C ("Hofmann's carbide") (12). According to other data, "Hofmann's carbide" is a ferrous oxide (13).

Decomposition of CO over Fe₂O₃ between 226° and 276° produced a mixture of Fe₂C and free carbon (14). When reacted with hydrogen, carbidic carbon changes to CH₄ in the range 225° to 290° and to free carbon between 280° and 320°. Decomposition of CO over iron (produced by hydrogenation of oxide at 280° to 290°) below 400° gave a mixture of Fe₃C and Fe₂C; above 400° the amount of carbidic carbon corresponded to Fe₃C. With iron prepared by reducing Fe₂O₃ at 247° to 262°, only Fe₂C could be obtained at 225°.

Contrary to the opinion of Sabatier (15), who considered possible an intermediate oxidation of iron by carbon monoxide,

$$Fe + CO \rightarrow C + FeO; \ FeO + CO \rightarrow CO_2 + Fe, \qquad (2)$$

and in agreement with other authors' data (5), iron was oxidized at higher temperatures by carbon dioxide produced during decomposition of CO (14). Below 324°, CO₂ has no effect on iron. Between 333° and 412°, 8 percent of the iron is oxidized, and between 465° and 513° 40 to 60 percent. Formation of Fe₃O₄ up to 560° and of FeO up to 655° had been proved earlier by X-ray analysis (12) and was the basis of the assumption of some scientists that iron oxides are intermediates in the decomposition of CO. Other authors (10, 16–18), who investigated the decomposition of CO on iron and Fe–Cu catalysts, noticed that the deposited carbon always contains iron or both iron and copper. This fact may be explained by deposition of carbon in the crystal lattice of the catalyst with intermediate formation of carbidic carbon, which rapidly diffuses through the lattice and changes to elemental carbon. The presence of copper in the carbon deposits, in experiments with Fe–Cu catalysts, indicates that carbide, not carbonyl, is the intermediate.

Treatment of precipitated iron with CO at 0.1 atmosphere and 325° caused intensive conversion to carbide (19). The maximum carbidic carbon content amounts to 4.6 percent, which corresponds to the optimum activity and stability of the catalyst at 15 atmospheres and 235°. After synthesis at 210° the carbidic carbon content decreases to 3.5 percent, remaining constant for months thereafter. After 550 days of operation, when the synthesis temperature had already risen to 285°, carbidic carbon had decreased to 1 percent, and elemental carbon amounted to 8 percent. The oxygen content, initially 0.6 percent, rose to 1.6 percent after 112 days and to 20 percent after 550 days.

An increase in the $CO:H_2$ ratio in the inlet gas and the presence of alkali in the catalyst contribute to increasing the rate of formation of elemental carbon. One would think that an increase of hydrogen in the gas should cause more rapid consumption of carbidic carbon during synthesis, on the hypothesis that "bulk carbide" is an intermediate in the synthesis. ("Bulk carbide" is in the crystal lattice, while "surface carbide" forms only a layer of surface atoms of carbon, which are connected with atoms of the metal on the surface.) This assumption is, however, questionable because of new data (20) obtained with radioactive C^{14} and on the basis of thermodynamic calculations of the synthesis of normal alpha-olefins (C_2–C_6) and n-paraffins (C_2–C_4) by reduction of Fe_2C at 227° and 327° (21).

The increased rate of carbon formation with decreased concentration of hydrogen in the inlet gas may be explained by some delay in the penetration of hydrogen into the lattice, the delay permitting diffusion of carbidic carbon through the lattice with formation of carbon-carbon bonds. With alkali in the catalyst, carbidic carbon diffuses even more readily.

Fe_2C is formed always and exclusively when precipitated, unreduced iron catalysts are treated with carbon monoxide at 0.1 atmosphere and 325°; the presence of copper in the catalyst increases the rate of carbide formation. This carbide, Curie point 265°, is slowly reduced with hydrogen at 230° to 240°. Another carbide, Curie point 380°, is obtained by reducing iron oxide at 250° and carburizing with CO at 220° (22). Such a pretreated catalyst has low activity in the synthesis. Both carbides, when heated above 300°, are transformed into cementite (Fe_3C).

In precipitated-iron catalysts, not subjected to CO treatment, the carbide content slowly changes during synthesis. After 120 hours of operation the $Fe_2C:Fe_3C$ ratio was 0.3; the catalyst passed through its maximum activity during this period. The higher the temperature of reaction or activation of the sample, the sooner this maximum is reached (23).

Braude and Bruns (24, 25) used a circulating system to study the hydrogenation of CO (in 1 CO:3.5 H_2) over iron, which was obtained by reducing synthetic magnetite at 400° during 36 hours. Fe_3O_4 had been prepared by burning technical iron (steel 1) in a stream of oxygen (26). The process was divided into two distinct stages. The initial rapid reaction was completed within the first 5 minutes, with total conversion of CO; the decrease in pressure equaled twice the initial partial pressure of CO. The second, very slow stage corresponded to hydrogenation of carbide with excess hydrogen.

Carbide formation, the authors thought, resulted from the rapid reaction of the first stage:

$$nFe + CO + H_2 \rightarrow Fe_nC + H_2O. \qquad (3)$$

This hypothesis was supported by the pressure change in the first stage, by formation of water as principal product, and because the amounts of CO_2 and CH_4 formed were much smaller than the amount of the reacted CO. The missing amount of carbon had accumulated in the catalyst. Oxygen contained in CO was completely converted to CO_2 and H_2O. The catalyst rapidly lost its activity and became entirely deactivated after 1 atom of carbon was deposited for each 4 atoms of iron. Carbon dioxide was formed in accordance with the reaction

$$nFe + 2CO \rightarrow Fe_nC + CO_2, \qquad (4)$$
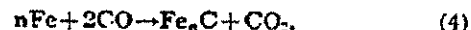
which is much slower than reaction 3. The apparent activation energies of reactions 3 and 4 were 15.5 and 6.4 kcal./mole, respectively.

The authors' claim that they observed rapid carbiding calls for better evidence. Braude and Bruns do not give any data concerning the chemical characteristics of the carbon in the catalyst but assume it to be carbidic. Apparently, however, much of it was free carbon, especially so in experiments at 240° to 350°, as shown both by the rapid decrease of catalytic activity and by the C:Fe ratio (1:4) observed toward the end of the reaction.

Normally, when free carbon is not formed, all iron is converted to carbide. Carbidic carbon readily diffuses into the interior of the lattice, whereas free carbon obstructs the catalyst surface. The very presence of such an unusually iron-rich Fe_4C "carbide" indicates that the reaction could not go to completion because the catalyst was covered with carbon. Apparently carbide, produced in small quantities at first, immediately began to catalyze reaction 1, and carbiding ceased. The extremely slow hydrogenation of deposited carbon also points in this direction. The iron catalyst employed in this investigation not only was not characteristic of a catalyst for the synthesis of hydrocarbons from CO and H_2 but also showed rather low activity in methane formation (25).

Thus, the authors' assertions are doubtful; that is, that (1) they "proved the formation of carbide by way of a reaction similar to the one postulated by Craxford, that is, as an intermediate of the carbon monoxide hydrogenation" (27, 28) (for cobalt catalyst; compare reactions 7 and 3); and (2) their data "make doubtful the conclusion by Eidus that carbide cannot be an intermediate in the hydrogenation of carbon monoxide on cobalt and nickel." (29).

Decomposition of CO over nickel is also attributed to catalytic action of the carbide. Passage of CO at 250° to 270° over metallic nickel, obtained by reducing its oxide with hydrogen between 275° and 285°, resulted in complete conversion to Ni_3C carbide (30). No free carbon was formed in the process. Between 270° and 380° to 420° the solid phase contained only Ni_3C and free carbon. Above 380° to 420°, Ni_3C was unstable and decomposed, with formation of nickel.

Ni_3C was assumed to catalyze decomposition of CO. In view of the stability of Ni_3C below 380°, its catalytic activity was assumed not to be connected with its decomposition. A higher labile carbide Ni_3C_x (probably Ni_3C_2) was considered to be formed, which dissociates into Ni_3C and free carbon. This higher carbide had been investigated by several scientists who arrived at conflicting results. Some indications point to the existence of a stable higher carbide (31), but this is questioned by others (32).

CO decomposition over carbonate-precipitated nickel and the mechanism of this reaction at 250° to 450° have also been studied lately (33). Such catalysts are not very active in this reaction. When supported on kieselguhr and promoted with thoria, however, nickel becomes quite active and is converted quantitatively to Ni_3C at 250°. With increasing temperature it decomposes progressively into metal and free carbon. At 450° a small amount of Ni_3C remains.

Cobalt was also investigated with respect to decomposition of CO and formation of carbides. CO was passed over cobalt and CoO at 270°; the decomposition of the labile carbide Co_2C_x produced Co_2C and elemental carbon (10). Later, Bahr and Jessen discovered that the product obtained in 500 hours by passing CO at 226° to 230° over cobalt, reduced from the oxide, contained 9.53 percent carbon, of which 9.22 percent was in the form of carbide (Co_2C contains 9.22 percent) (34). This carbide proved unstable above 275°. It was hydrogenated between 240° and 250° to CH_4 and metal, while free carbon was hydrogenated in the range 350° to 400°.

X-ray analysis shows that the easily hydrogenated carbon, which is produced when cobalt reacts with CO at 225° to 300°, forms a solid solution in alpha-Co; (35) between 450° and 600° carbon combines with cobalt to form a distinct crystalline carbide isomorphous with cementite (Fe_3C). Later, however, also by the X-ray method, the easily hydrogenated carbon was found not to be held in solid solution but as Co_2C with its own crystal structure, distinct from alpha- or beta-Co (36). The difficultly hydrogenated free carbon appears as finely divided carbon crystallites.

Craxford and Rideal used a closed system to measure the reaction of CO with 100 Co–18 ThO_2–kieselguhr between 150° and 250°, as well as the rate of subsequent hydrogenation of the solid products (28). The process was divided into two stages. The second stage began after several hours and proceeded appreciably slower (independent of pressure, above 30 cm. Hg) than the first. The rate of volume (pressure) change was taken as the rate of carbide formation,

$$2Co + 2CO \longrightarrow Co_2C + CO_2. \qquad (5)$$

the first stage (apparent activation energy, 10 kcal./mole) being attributed to reaction on the "active parts of the catalyst surface" and the second (apparent activation energy, 18 kcal./mole) to reaction in the bulk of the metal.

They were the first to consider "surface carbide" along with the recognized "bulk carbide." Weller and others remarked on the difficulty of distinguishing (or noticing mutual transition, Y. T. Eidus) between "surface" carbide and adsorbed CO (37).

They (28) did not indicate, however, whether they thought that free carbon (34) forms simultaneously with carbide when CO is decomposed over cobalt alone. Reduction of carbide by hydrogen on Co–ThO_2–kieselguhr proceeded at a rather low temperature (140°) and considerably faster rate than its formation.

Zelinskii and Eidus (38) were the first to investigate (in a flow system) carbiding of precipitated Co–ThO_2–kieselguhr with CO at 190° to 270°. They followed weight changes of the solid phase to determine rates. Two processes were observed—carbide formation and deposition of free carbon. The readily reduced carbidic carbon (at 200°) was determined by weight decrease after hydrogenating at the same temperature to constant weight. Free carbon was determined by difference between total and carbidic carbon.

The rates of carbiding and carbon deposition depended on temperature; the former reaction predominated at 190° to 210°. The rate of carbon deposition, negligible in this range, increased rapidly with rise of temperature. At 270° about 5 gram-atoms of free carbon was deposited for every gram-atom of cobalt. In the range 190° to 240° the atomic ratio of carbidic carbon to cobalt remained constant and corresponded to Co_2C. At 270° this ratio corresponded to a carbide poorer in carbon, which appears to be formed by decomposition of Co_2C.

The Soviet chemists were thus the first to show that Co_2C is formed when CO reacts with Co–ThO_2–kieselguhr at synthesis temperature.

They also showed that carbides catalyze carbon formation and that carbide formation

proceeds at an appreciably faster rate on promoted catalyst than on reduced cobalt and at a lower temperature (192° instead of 225°) (34). Hydrogenation of carbide also occurred at lower temperatures (190° to 210° as against 240°), and the rate of reduction was about 4 times the rate of its formation (34).
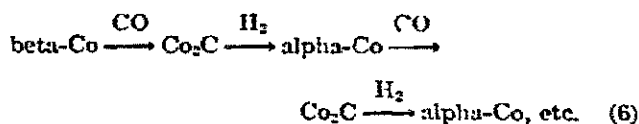
Thus, the presence of ThO_2 and kieselguhr hastened the formation and reduction of Co_2C, as later confirmed by Craxford (27). He showed that Co, 100 Co:18 ThO_2, 1 Co:1 kieselguhr, 100 Co:18 ThO_2:100 kieselguhr, and 100 Co:21 ThO_2:100 kieselguhr all have different activity in carbiding at 200°, according to reaction 5, and that ThO_2 and kieselguhr speed this reaction.

The more active among these catalysts, for carbide formation, are 100 Co:18 ThO_2 and 100 Co:18 ThO_2:100 kieselguhr, in this sequence. All these catalysts are, however, equally effective in hydrogenating ethylene at 20° (and therefore, in the author's opinion, have almost equal specific surfaces). Hence neither ThO_2 nor kieselguhr has any special activating effect on the hydrogenation of double bonds.

In hydrogenating carbide to methane, however, 100 Co:18 ThO_2:100 kieselguhr, next to cobalt, is one of the least effective catalysts, even though it is one of the more active ones in the synthesis of hydrocarbons. Hence ThO_2 in Co–ThO_2–kieselguhr was thought to lower the rate of hydrogenation of cobalt carbide to methane (by comparison with cobalt). In other words, ThO_2 in some unknown way inhibits the hydrogenating activity of cobalt. ThO_2 and kieselguhr had been considered to be specific promoters of carbide formation and reduction. However, the acceleration of carbiding could also be explained by the fact that cobalt containing ThO_2 and kieselguhr has a greater specific surface.

Active precipitated catalysts, such as 100 Co:18 ThO_2:100 kieselguhr and Hall's 100 Co:6 ThO_2:12 MgO:200 kieselguhr (39) contained beta-Co with a face-centered cubic lattice after complete hydrogenation for 42 to 84 hours at 400° (36). Conversion to alpha-Co with a hexagonal close-packed lattice occurred very slowly at 340° to 380° (40). At lower temperatures and particularly in the synthesis range (170° to 210°), beta-Co was metastable.

Upon reacting at 208° with the above catalysts, CO converted beta-Co completely to Co_2C, which, on the basis of the previous results (36), was identified by X-ray analysis. Carbide formation was about 10 times as rapid in the catalyst containing MgO. Hydrogenation at 208° converted this carbide to methane and stable alpha-Co. With a catalyst containing MgO, formation of free carbon also took place. At 300° beta-Co may remain in reduced Co–ThO_2–kieselguhr for at least a week without changing to alpha-Co. Both varieties of cobalt reacted with CO to form carbide at approximately the same rate, as shown by the possibility of reproducing the following cycle at 210° after reducing the catalyst at 400°:

$$\text{beta-Co} \xrightarrow{\text{CO}} Co_2C \xrightarrow{H_2} \text{alpha-Co} \xrightarrow{CO}$$

$$Co_2C \xrightarrow{H_2} \text{alpha-Co, etc.} \quad (6)$$

The rate of carbiding was much lower than its hydrogenation. ThO_2 and kieselguhr did not play any noticeable part in these conversions.

According to the above data the carbides of cobalt, nickel, and iron are intermediates as well as catalysts in the decomposition of CO. The old ideas that metals themselves are such catalysts (14) are heard only rarely now.

CARBIDE AS AN INTERMEDIATE IN THE SYNTHESIS

The problem of carbide as an intermediate in the synthesis of hydrocarbons, which arose during examination of the synthesis mechanism (3), has not yet been resolved satisfactorily. Accumulation of "bulk carbides" during synthesis was considered proof that these carbides are intermediates (28). But all attempts to obtain more direct and convincing proofs of this theory have failed.

The carbide theory would have been proved, if, for example, a carbide had been formed with CO under synthesis conditions which, treated

with hydrogen at the same temperature, would have yielded higher hydrocarbons (42). Such experiments were carried out by Fischer and Koch on Co–ThO_2–kieselguhr with negative results (43).

Considering that carbide may inhibit further reaction of CO with metal (Co) by covering the catalyst surface, Zelinskii and Eidus made similar tests of the carbide theory on the same sample (44). They modified the experiment by alternately passing over the catalyst in relatively rapid succession CO, N_2, H_2, N_2, CO, etc.,

which participated in the synthesis separately. Again, no liquid hydrocarbons could be observed.

Passing CO over Co–ThO₂–kieselguhr caused poisoning; in other words, formation of carbide inhibited the synthesis of hydrocarbons from CO and H₂ (44). In comparing rates of (1) formation of carbide with CO, (2) hydrogenation of carbide, and (3) synthesis of hydrocarbons with CO+H₂ on the same Co–ThO₂–kieselguhr catalyst, Zelinskii and Eidus found ratios of about 1:4:10 (44). They therefore concluded that carbide, formed when CO reacts with cobalt, cannot be an intermediate in the synthesis, because the overall rate cannot exceed the rate of an intermediate step.

Under entirely different conditions and by a different method (pressure decrease in a static system), Craxford observed similar ratios of rates of carbide formation, reduction, and synthesis on the same catalyst (28). Since such ratios conflict with the carbide theory, he added the assumption that intermediate carbide is formed not in accordance with reaction 5,

$$2Co + 2CO \rightarrow Co_2C + CO_2. \qquad (5)$$
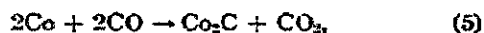
but—in the presence of H₂ and at a faster rate—according to reaction 7

$$2Co + CO + H_2 \rightarrow Co_2C + H_2O. \qquad (7)$$

However, no qualitative difference is known between carbides obtained in each reaction, nor is supporting experimental evidence available.

On the basis of their own data, Zelinskii and Eidus arrived at completely different conclusions (44):

(1) CO poisons the Co catalyst; that is, it inhibits the synthesis of hydrocarbons from CO and H₂.

(2) The carbide formed when CO reacts with this catalyst is neither an intermediate nor the catalyst for gasoline formation.

Six years later, American chemists of the Bureau of Mines, without reference to the above investigations and conclusions (38, 44), repeated these conclusions word for word in their own study (37). They wrote: (1) "Evidence is presented that for cobalt catalysts, bulk cobalt carbide is neither an intermediate in the Fischer-Tropsch synthesis nor a catalytically active substrate for the synthesis"; and (2) "the presence of extensive amounts of carbide in cobalt catalysts severely inhibits the Fischer-Tropsch synthesis." Their procedure and results are very similar to those of the Soviet authors.

X-ray analysis had also shown that "bulk carbide" is not an intermediate in the synthesis on cobalt catalyst (37). Co₂C formed with CO

before synthesis was still present after synthesis; when the catalyst was not pretreated with CO, Co₂C could not be detected after synthesis. Besides, as already shown above in the cycle of transformations, beta-Co in a catalyst freshly reduced at 400° is transformed by way of Co₂C into alpha-Co. However, the catalyst contained only beta-Co after synthesis, like freshly reduced catalyst before synthesis. This proves conclusively that (considering the accuracy of the method) at least 95 percent of the cobalt was not converted to intermediate "bulk carbide" during synthesis.

Recently Craxford (45) also stated that carbide played no part in the synthesis of hydrocarbons with cobalt catalysts now in use. Carbide is formed from a normal or slightly modified cobalt metal lattice into which single carbon atoms diffuse. Since Craxford's catalysts apparently contained separate layers of cobalt atoms with an arrangement based on the structure of cobalt silicate instead of that of metallic cobalt, formation of "bulk carbide" must be considered impossible.

Because a comparison of carbon formation and synthesis kinetics helps in understanding the role played by carbide in the synthesis, Eidus investigated in detail Co–ThO₂–kieselguhr, Ni–Mn–Al₂O₃–kieselguhr, and Fe–Cu–ThO₂–K₂CO₃–kieselguhr in 1944–46. A new combination method was used by him, permitting determination of the reaction rate (catalyst activity) and its changes at any time. The change was determined in a flow system, while the rate was measured in a static system by changes in pressure resulting from gas contraction (46).

Contraction during reaction is proportional to the yield of hydrocarbons and therefore can be used to measure reaction rates (47), keeping in mind the circumstances under which this relationship is upset (46, 48).

Kinetics of carbiding and synthesis were compared not only with the whole heterogeneous catalyst but also with its components and their combinations; this permitted elucidation of the role of these components. Such a study was made, for example, on Fe–Cu–ThO₂–K₂CO₃–kieselguhr with CO (49), CO₂ (50), and synthesis gas (49).

Only those iron samples were catalytically active that contained Fe and Cu and also either ThO₂ or K₂CO₃; addition of both substances caused a sharp increase in activity. The relative reaction rates are shown in table 1.

This method of determining the role of single components was applied 2 years later by Craxford to cobalt catalysts in a static system (27) and 4 years later by American scientists, also to cobalt catalysts (51).

TABLE 1.—*Comparison of rates of reaction of various gases over iron catalysts*

Catalyst	Inlet gas					
	CO_2		CO		$CO+H_2$	
	Initial rate	Rate after 2 hr.	Initial rate	Rate after 1 hr.	Initial rate	Rate after 1 hr.
100Fe : 25Cu : 2ThO₂ : 100 kieselguhr	0. 22	0. 06	0. 32	0. 23	0. 21	0. 25
100Fe : 25Cu : 2K₂CO₃ : 100 kieselguhr	. 30	. 23	. 37	. 30	. 61	. 82
100Fe : 25Cu : 2ThO₂ : 2K₂CO₃ : 100 kieselguhr	. 9	. 50	1. 23	. 5	1. 25	1. 33

Table 1 shows that the initial rates of carbiding and synthesis are quite close for Fe–Cu–ThO₂–K₂CO₃–kieselguhr. This fact does not exclude carbide as an intermediate in the synthesis on iron catalysts.

A study of cobalt and nickel catalysts led to entirely different results. In support of his previous data (44), Eidus (29) found that the rate of synthesis exceeds considerably the rate of carbiding on these catalysts (this relates to initial rates, too). Such a ratio of rates excludes carbide as an intermediate in the synthesis on cobalt and nickel catalysts.

A similar kinetic investigation of carbiding and synthesis on Co–ThO₂–kieselguhr was repeated a year later by Weller, who used a circulating gas system and froze the reaction products in liquid nitrogen, while determining the rate by the contraction of volume (52). Two stages of carbiding were observed: (1) An initial rapid stage during the first minutes and (2) a slower, steady rate over 20 to 150 minutes. Within the range 8 to 45 cm. Hg, the pressure dependence of the second, steady rate may be expressed by

$$r = kp^n, \text{ where } n = 0.20\text{–}0.26. \tag{S}$$

The equation shows that the impact of CO molecules on the surface (to form a layer of adsorbed CO or to react with such a layer to produce CO₂) has no limiting effect on the rate; otherwise, one would expect its pressure dependence to be linear.

According to Craxford and Rideal (28), the rate of the second stage is independent of pressure above 30 cm. Hg but diminishes below 30 cm. with increase in pressure.

Weller also found that Co₂C is hydrogenated much more rapidly than it is formed (52). If carbide formation and reduction occur with diffusion of carbon atoms through the metal lattice, this relationship of rates indicates that diffusion of carbon is not rate-determining.

Weller compared his kinetic data with those of Zelinskii and Eidus (38, 44) and of Craxford and Rideal (28), as shown in table 2; all experiments reported there were carried out at 200°.

Weller points out that his kinetic data are in reasonable agreement with those of Zelinskii and Eidus. The rates found by Craxford and Rideal were much lower due to the inhibiting effect of CO₂, produced during carbide formation and not eliminated from the static system. Weller further indicates that Zelinskii and Eidus obtained the first point on the kinetic curve after 5 hours of carbiding and that the initial rate was not measured (38). This remark is not entirely justified, since he did not take into consideration Eidus' later work (29), which appeared 1 year before Weller's work (52). It shows (see ref. 29, tables 1 to 3) that, when CO reacts with cobalt and nickel catalysts between 190° and 200°, the ratio of the initial rate to that after 3 hours is 4.4. Consequently, the rate of stage I is 185, as shown in table 2 in parentheses.

TABLE 2.—*Rates and activation energies of carbiding and synthesis over cobalt catalysts*

Reaction	Reference	Rate, 10⁴ gm. C/gm. Co-hr.		Apparent activation energy, kcal./mole	
		Stage I	Stage II	Stage I	Stage II
Carbiding	(28)	35 (1st min.)	0.8 (after 2–3 hours)	10. 0	18. 0
	(38, 44)	(185) (29)	42 (first 5 hours)		14. 8
	(52)	1,000–2,200 (1st min.)	60–65 (20–150 min.)		31. 0
Synthesis	(28)	280		0. 5	
	(38, 44)	450			
	(52)	560		26. 5	

The rate of formation of carbide in stage II, which all authors identify as "bulk carbide," is approximately one-tenth the rate of synthesis. On the other hand, the rate of the initial reaction of CO with the catalyst is comparable with the rate of synthesis according to Weller and is lower than that rate according to Eidus, and Craxford and Rideal. The last authors relate this process to the formation of "surface carbide" about which, however, very little is known ("chemisorbed C atoms") (45), and the formation of which is difficult to distinguish from CO adsorption

One important conclusion from the above data was firmly established by Zelinskii and Eidus 7 years ago, that is. that carbide is not an intermediate in the synthesis with cobalt and nickel (44).

OXYGENATED COMPOUNDS AS INTERMEDIATES IN THE SYNTHESIS

The theory of the formation of intermediate oxygenated organic compounds, particularly methyl alcohol, in the synthesis (53) suggested investigating the behavior of some of the simplest oxygenates under conditions of the synthesis. Methyl and ethyl alcohols and formic acid, investigated by Eidus (54), were converted over cobalt into a synthol-type mixture of hydrocarbons. This conversion did not proceed directly but by way of an intermediate decomposition into a mixture containing CO and H_2 which, upon further reaction only, was synthesized to hydrocarbons. Methyl alcohol was not an intermediate in the synthesis. Thus, the theory of intermediate formation of oxygenated compounds appears to have little value.

Views close to those of Elvins (55) have lately been expressed. that carbonyls are intermediates in the synthesis (56). Such a mechanism, acceptable in the oxo synthesis, is inadequate for the synthesis of hydrocarbons. CO chemisorption is a stage preliminary to carbonyl formation. But under synthesis conditions cobalt atoms in contact with CO are not removed from the lattice (45).

METHYLENE RADICALS AS INTERMEDIATES IN THE SYNTHESIS

The hydrocarbons formed from CO and H_2 are considered to be the products resulting from polymerization of unstable methylene radicals adsorbed on the catalyst surface and formed upon hydrogenation of carbides (3). Considering our knowledge of carbide as an intermediate. we must examine the theory of CH_2 intermediates separately and independently of carbide formation, because experimental verification of this theory is of interest.

Butlerov thought of the possible existence of CH_2 radicals (57). To obtain them in the free state, he reacted methylene iodide with copper in the presence of water in sealed tubes at 100°. These CH_2 radicals, however, immediately combined with each other to give ethylene and small amounts of its homologs.

Orlov used Butlerov's concept of CH_2 radicals to explain the mechanism of catalytic hydrogenation of CO (58). He proposed the following scheme of C_2H_4 formation from CO and H_2 in the presence of Ni-Pd catalyst:

$$CO + 2H_2 \rightarrow CH_2 + H_2O, \tag{9}$$

$$2CH_2 \rightarrow C_2H_4. \tag{10}$$
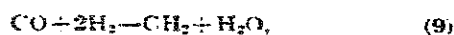
Zelinskii and Eidus set themselves the task of verifying this theory experimentally (59)

If it is correct, one would expect that a tracer hydrocarbon should be methylated by CH_2 radicals to the nearest homolog. Making sure that no toluene was present, the authors introduced benzene into the synthesis zone and found that it was partly transformed into toluene. Further experiments established that CH_2 radicals, detected during methylation of benzene,

$$C_6H_6 + CH_2 \rightarrow C_6H_5CH_3, \tag{11}$$

evolved from CO and H_2 but not from benzene or the cyclohexane derived from it (44). The latter may undergo complete decomposition to CH_2 radicals,
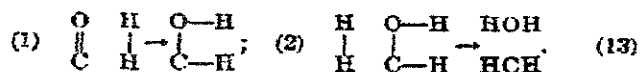
$$C_6H_{12} \rightarrow 6CH_2, \tag{12}$$

in the presence of $Ni-Al_2O_3$, as had been shown by Zelinskii and Shuykin (60).

Thus. the first experimental demonstration had been given that CH_2 radicals are actually formed in the synthesis.

Recently, Zelinskii stated that perhaps natural solid paraffins as well are formed from CH_2 radicals (61).

The experimental data led Eidus (54) to the conclusion that CH_2 radicals are formed along with water on cobalt and nickel catalysts by

hydrogenation of unstable CHOH, which, in turn, forms when CO reacts with H_2, all adsorbed on the catalyst surface:

$$
(1)\ \begin{matrix} O \\ \| \\ C \end{matrix}\ \begin{matrix} H \\ | \\ H \end{matrix} \begin{matrix} O-H \\ \to \\ C-H \end{matrix}\ ;\quad (2)\ \begin{matrix} H \\ | \\ H \end{matrix}\ \begin{matrix} O-H \\ | \\ C-H \end{matrix} \to \begin{matrix} HOH \\ \\ HCH \end{matrix}. \tag{13}
$$

In the synthesis over iron CH_2 is probably formed by hydrogenation of carbides (29, 49).

Karzhavin confirmed that, based on the heat generated by bond dissociation on a nickel catalyst surface, the HCOH complex is possible, while the formation of carbide during synthesis is doubtful (62). Myddleton also favored the mechanism of dual attachment in the process of CH_2 radical-formation on cobalt, while considering it unobtainable with iron (63). Simultaneously and independently Hamai also proposed a similar mechanism of CH_2 radical-formation (64):

$$
Co-Co(-C=O)-Co \to Co-Co(-HCOH)-Co \to
$$
$$
Co-Co(CH_2)-Co-. \tag{14}
$$
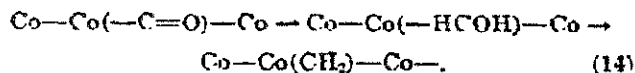
In his view, however, this process occurs not only on cobalt and nickel but also on iron; and oxygen always passes from CO to H_2O. The occurrence of CO_2 instead of H_2O in the products of reaction on iron was attributed to the water-gas shift,

$$
CO + H_2O \rightleftharpoons CO_2 + H_2. \tag{15}
$$
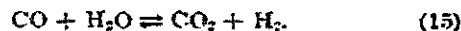
Eidus had shown that, according to the thermodynamics of reaction 15, one should expect conversion of H_2O to CO_2 not only on iron (at 230° to 260°) but with still greater probability on cobalt and nickel (190° to 200°) (50). This view, however, conflicts with experimental evidence. Craxford and Rideal have experimentally shown on Co–ThO$_2$–kieselguhr that "* * * in synthesis of hydrocarbons the Fischer catalyst must be inactive for the water-gas shift reaction although normally it is a most effective catalyst for it." (28)

Eidus in 1945 said that "it seemed quite possible and deserving experimental verification that iron, like cobalt, remains inactive for the water-gas shift during synthesis." (50)

That such a possibility was not excluded and that CO_2 might occur directly on iron as a result of carbide formation, for example, was indicated by the comparative study of carbide formation and synthesis kinetics (29, 49) and by several peculiarities distinguishing iron from cobalt and nickel. The first among these peculiarities is the necessity to promote Fe–Cu catalysts with alkali. As already shown by Eidus, these promoters cause CO_2 to react with the catalyst surface (table 1) and appreciably increase its activity in carbide formation and synthesis (50). Notwithstanding the small amount (1 percent) of K_2CO_3, alkali appears to accumulate on the

catalyst surface, taking up a substantial part (30–40 percent) of the active area. Another important distinction between iron catalyst and cobalt and nickel catalysts consists in the difference of stoichiometry of the synthesis reaction and in the fact that CO_2 is predominant in the first case, H_2O in the second (we are not concerned here with iron catalysts on which water is the main byproduct in the synthesis nor with the conditions, such as increase of pressure, which bring this about).

Thus, two possible schemes may apply to iron: (1) Carbide formation in accordance with reaction 4, giving CO_2, and hydrogenation of carbide to CH_2 radicals; (2) formation of CH_2 radicals and H_2O in accordance with reaction 13 and further conversion of H_2O to CO_2 following reaction 15.

Either of these schemes presumes a difference in the total course of the reaction, as well as a difference of the catalytic properties of iron on one hand and cobalt on the other.

If correct, the second scheme would presume an entirely different relation of this group of catalysts with respect to reaction 15.

Recent data show that iron can catalyze the water-gas shift under synthesis conditions. Bashkirov, Kagan, and Kryukov showed that water introduced into the synthesis zone in the presence of iron readily reacts with CO according to equation 15, while the synthesis of hydrocarbons continues simultaneously (65). The rate of reaction 15 many times exceeds the rate of synthesis. A pronounced difference is thus revealed between cobalt and iron with respect to reaction 15. It would have been of great interest to test, under the same conditions, Craxford and Rideal's finding about the inactivity of cobalt in reaction 15 during synthesis (28).

The apparent activation energy of the synthesis on iron (28.7 kcal./mole), determined by Eidus (49), is quite close to the value determined 2 years later by Weller (52) and other American researchers (66) for cobalt, 26.5 and 24–27 kcal./mole, respectively.

The most important stage in the synthesis, after CH_2 radicals are formed, is their polymerization on the catalyst surface with formation of olefins,

$$
nCH_2 \to C_nH_{2n}. \tag{16}
$$

which, depending on the hydrogenating capacity of the catalyst and on the H_2 concentration, are further hydrogenated to a greater or lesser degree to paraffins,

$$
C_nH_{2n} + H_2 \to C_nH_{2n+2}. \tag{17}
$$
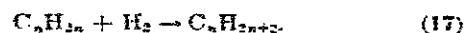
The mechanism of polymerization of CH_2 radicals has been little studied experimentally. Adsorbed CH_2 radicals have been assumed to

combine with each other to form a giant hydrocarbon chain of CH$_2$ groups (28), each of which remains in contact with the catalyst surface (1).

The existence of such a long chain, all links of which are in contact with surface centers of cobalt or nickel, is, however, in conflict with the principle of conservation of valency angle in catalysis (67, 68). In accordance with this principle, another scheme involving CH$_2$ radicals was proposed (69). It assumes that hydrocarbon chains of chemisorbed CH$_2$ radicals are maintained in 2-point contact with the surface by 2 adjacent carbon atoms. Polymerization of CH$_2$ starts with the combination of 2 of such groups, adsorbed at a distance of closest packing, and leads to formation of an ethylene molecule adsorbed by dual attachment, in keeping with the mechanism according to which a double bond changes to a single bond (70).

One of the carbon atoms of the adsorbed ethylene molecule is joined by a new CH$_2$ group, which is also adsorbed at a distance of closest packing. In the process, a carbon atom of ethylene is desorbed from the surface and attached to a hydrogen atom which migrated from the first carbon atom. A propylene molecule is thus formed, which is also adsorbed by dual attachment at adjacent atoms on the catalytic surface. In keeping with the same mechanism, further attachment of new CH$_2$ groups follows, with consecutive formation of butylene, amylene, and higher olefins. The hydrocarbon chain grows at one end with the formation of alpha-olefins, which, as a result of a secondary process, may isomerize with a shift of the double bond (68).

This mechanism of polymerization shows the unique position of ethylene in the homologous series of olefins, since both its CH$_2$ groups may be attached. After ethylene has been formed by 2 CH$_2$ radicals, its growth by attachment of a new CH$_2$ group may therefore be assumed to proceed much faster than growth of its homologs. This assumption agrees with experiment (71), showing that relative and absolute quantities of ethylene are negligible in synthesis products, although its formation is thermodynamically favorable under these conditions (63).

This mechanism leads one to expect that ethylene added to CO and H$_2$ would readily participate in CH$_2$ polymerization. That conclusion is partly confirmed by the work of Smith, Hawk, and Golden, who observed an increased yield of liquids on Co–Cu–MnO at atmospheric pressure and 204° to 205°, when 25–35 percent ethylene was added to water gas (72). On the average, the yield of liquids was increased from 25 to 50 ml./m³ of synthesis gas. The products contained 25–35 percent oxygenates. These results, however, appear inadequate

in the light of the above conclusions, because the yield with ethylene was far below normal yields obtained with CO–H$_2$ mixtures. In addition, the net increase also appears insufficient.

Catalytic hydrocondensation of CO with olefins, discovered by Zelinskii, Eidus, and Puzitskii (73–76), and hydropolymerization of olefins under the influence of CO, discovered by Zelinskii, Eidus, and Ershov (76, 77), fit into the above mechanism. These reactions are very similar to polymerization of methylene radicals in the presence of hydrogen and confirm their important role in such processes.

Discovery of these reactions allows the conclusion that methylene polymerization, starting with the combination of two CH$_2$ groups to form adsorbed ethylene, is a continuous combination of CH$_2$ groups with the simplest olefin molecules adsorbed by dual attachment at adjacent atoms on the catalytic surface. This conclusion explains the mechanism of that stage of the synthesis of hydrocarbons from CO and H$_2$.

Doubly attached ethylene is the usual form of the CH$_2$ dimer on the catalytic surface. The catalytic polymerization of single CH$_2$ radicals has also been studied. Diazomethane and ketene appeared to be suitable starting materials; their photochemical and thermal decomposition into CH$_2$ groups had already been proved (78–81), (1). They were expected to undergo a similar decomposition in contact with a catalyst, except that the adsorbed CH$_2$ radicals would further polymerize to a mixture of hydrocarbons similar to synthol.

While I was investigating the catalytic decomposition of ketene, the results of a similar investigation were published (82). Ketene and hydrogen, when passed over Co–ThO$_2$–kieselguhr at 210°, yielded the expected gasolinelike hydrocarbons, amounting to 21.8 percent of all products. Also obtained were 2.8 percent CH$_4$, 2.7 C$_2$H$_4$, 3.8 C$_3$H$_6$, and 3.6 percent solid paraffin. The CO content in the products was 64.2 percent. Altogether, 7.35 l. hydrogen and 20 ml. liquid ketene were passed over the catalyst. However, the authors drew the dubious conclusion that ketene is an intermediate in the synthesis. Under synthesis conditions one can hardly expect CH$_2$ groups to combine with CO to produce ketene. In addition, if such a reaction were taking place, the large amounts of reaction water, characteristic of synthesis over cobalt, should have been accompanied by large yields of acetic acid, which was not the case. Examination of the behavior of diazomethane in the presence of the above catalyst would be of even greater interest, because inert nitrogen would be formed instead of CO, which complicates the picture.

With respect to termination of the synthesis, a recent idea is that a polymerization-depolymerization equilibrium exists (45, 83), based on further development of the concept of the formation of giant molecules from CH_2 radicals (28). The assumption is that some of the chemisorbed CH_2 radicals are in transition from single radicals to a giant molecule. At the same time, adsorbed hydrogen is considered to be a principal chain terminator (84–89).

According to the theory of intermediate formation of CH_2 in the synthesis, the only chain builders are CH_2 radicals. Karzhavin and Polyakin (62) and Robinet (90), however, assumed that CO and H_2 also participate directly.
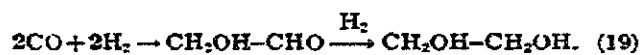
Karzhavin and Polyakin, without taking into account the principle of conservation of valency angles in catalysis (67), considered polymerization of CH_2 radicals on cobalt and nickel not feasible because the atomic spacing for closest packing is 2.49–2.5A., and the C–C bond in hydrocarbons is 1.5A. Actually, however, precisely these distances correspond to each other as concerns the ease of combining two CH_2 radicals (67, 68). They postulated that participation of MnO was indispensable in the synthesis on Ni–MnO–Al$_2$O$_3$–kieselguhr. According to their mechanism, two CH_2 radicals adsorbed on nickel are combined by means of a CO molecule adsorbed on MnO. In the process, the oxygen from CO and one hydrogen atom from each CH_2 form water, which is adsorbed on Al_2O_3; as a result, allene biradicals occur:
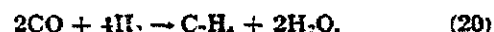

$$(18)$$
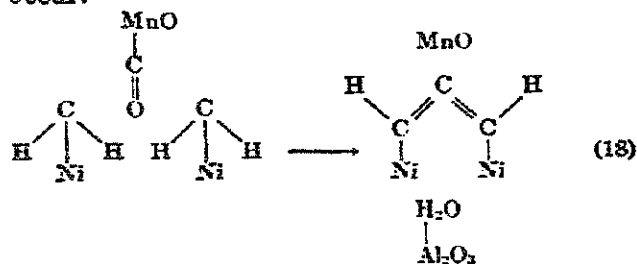
These biradicals react further with H_2, CO, and CH_2 radicals.

Robinet assumed three types of CO hydropolymerization (90):

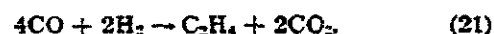1. Hydropolymerization without formation of fragments, leading to formation of oxygenates at high pressures:

$$2CO + 2H_2 \rightarrow CH_2OH-CHO \xrightarrow{H_2} CH_2OH-CH_2OH. \quad (19)$$

2. Hydropolymerization with removal of H_2O:

$$2CO + 4H_2 \rightarrow C_2H_4 + 2H_2O. \quad (20)$$

3. Hydropolymerization with removal of CO_2:

$$4CO + 2H_2 \rightarrow C_2H_4 + 2CO_2. \quad (21)$$

He considered the synthesis of hydrocarbons from CO and H_2 to be a complex hydropolymerization with removal of H_2O and CO_2 after condensation. At first, a primary complex is formed on the catalyst, which disintegrates mainly into CH_4, H_2O, and CO_2. Under the condensing influence of the catalyst, however, the complex grows, not only because of the activity of CO and H_2 but also because of the free radicals, which occur simultaneously on different centers.

Thus, in accordance with these views, what is really taking place is not a polymerization of radicals but a kind of copolymerization.

However, no experimental evidence exists in support of this theory. Hydrocondensation of CO with olefins does not occur in the absence of H_2 (75); this indicates the necessity of prehydrogenating CO.

Even less probable seems the growth of long carbon chains directly from CO groups of metal carbonyls, with subsequent hydrogenation to CH_2 and formation of hydrocarbons (C_9H_{18}, for example) (55).

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