Physico-Chemical Investigations on Catalytic Mechanism. II. Note on The Fischer-Tropsch Synthesis of Hydrocarbons with Special Reference to its Reaction Mechanism.

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Introduction. With increasing demands for technological products, as well as from the theoretical interest in hydrocarbon chemistry in general, the synthesis of suitable hydrocarbons, especially in the line of fuel industry in the country where the sources of natural oil are lacking has become one of the most vital importance in the present time, especially, since the first publication of Fischer and Tropsch⁽¹⁾ was announced.

Fischer and his coworkers ever since have contributed much in establishing this into industrial scale, and besides many reports have been contributed from Professor Kita's laboratory in our country, but as far as its reaction kinetics and mechanism are concerned, the existing literatures is practically none, or at least very meagre.⁽²⁾

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(1) *Ber.*, **56** (1923), 2428.
Brenn.-Chem., **4** (1923), 276, **5** (1924), 201 (Synthol); *Brenn.-Chem.*, **7** (1926), 97, 299; *Ber.*, **59** (1926), 830, 832, 923.

(2) (a) S. R. Craxford, *Trans. Faraday Soc.*, **35** (1939), 946.
(b) E. F. G. Herington and L. A. Woodward. *Trans. Faraday Soc.*, **35** (1939), 958.

Considering such a status, we have undertaken some aspect of this investigation so as to discuss the reaction mechanism of Fischer-Tropsch synthesis of hydrocarbons and also to select good and suitable catalyst to proceed the above mentioned synthesis very effectively.

Especially the fact that the word "Catalysis" according to Schönbein, is a "Synonym" for ignorance, truly points out the exact status of the field of catalytic investigations; however, at present some noticeable progress has been made by various workers. We are not yet to be satisfied with the present condition, and we feel that there should be much done among experimentalists as well as theoreticians in this field of vital importance.

These in mind, we have carried out our experiments; the present purpose of this paper is to discuss briefly the various mechanisms so far proposed especially in reference to the recent papers of Craxford, of Herington and Woodward, and of Kodama in connection with our new mechanism recently proposed(3) in detail.

According to Craxford(2a), the primary step in this synthesis is the alternate formation and reduction of cobalt carbide to give CH_2 group, as:

$$2Co + CO + H_2 \rightarrow Co_2C + H_2O \qquad (1)$$

and with the chemisorbed hydrogen, these methylene groups are being hydrogenated into CH_4; if the formation of carbide is more rapid than its reduction, there will be very little chemisorbed hydrogen on the surface, and the CH_2 group will link to form long chains. Furthermore, the products formed are broken off as long chains on the surface by the action of the chemisorbed hydrogen. When CO is adsorbed in the outer adsorption layers and not in direct contact with the catalytic surface, its reduction leads to compounds containing oxygen, rather than hydrocarbons.

While Herington and Woodward(2b) proposed that there are two types of catalytic surfaces, namely Type A (probably cobalt carbide) which is responsible for the formation of the CH_2 groups which polymerize to the long chain hydrocarbons and Type B (probably bare cobalt metal) which through the agency of hydrogen, is responsible for the liberation of the observed products from the catalyst surface. During the reaction when (besides water) only gaseous products are formed, the centers of Type B predominate over those of Type A whereas, when liquid and solid products are produced the reverse is true.

A recent paper by Kodama and his coworkers(2c), proposed the mechanism of benzine synthesis as follows:

Firstly,

$$CO + 3M = M_2C + MO \qquad (2)$$

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(2) (c) S. Matsumura, K. Tarama and S. Kodama, *Sci. Paper of Inst. Phys.-Chem. Research* **37** (1940), 302.

(d) B. Jerofejew, A. Runtzo and A. Walkowa, *Acta Physicochim.* **12** (1940), 111.

(e) F. Fischer and H. A. Bahr, *Gesamm. Abh. Kennt. Kohle,* **8** (1929), 255; O. C. Elvins and A. W. Nash, *Fuel,* **5** (1926), 263; *Nature,* **118** (1926), 154; O. C. Elvins, *J. Soc. Chem. Ind.,* **46** (1927), 473; D. F. Smith. C. O. Hawk and P. C. Golden, *J. Am. Chem. Soc.,* **52** (1930), 3221.

(3) S. Hamai, *J. Chem. Soc. Japan,* **62** (1941), 516.

and then atomic hydrogen acting on M_2C to give CH_2 and finally the longer chain hydrocarbons. As far as CO is considered it seemed quite improbable i.e., CO at the surface of catalyst with excess of H_2, Co is practically in reduced state for complete reduction of Co below 200°C. and if CO is present, reduction temperature is even lower⁽⁴⁾.

Such reaction mechanism as Eq. (2) is another way of stating that carbon monoxide, at the surface of metal, is ruptured, and one of the components, the carbon remains as Co–C linked together (cobalt carbide) and the other component, oxygen, linked to the adjacent metal surface forming oxide of the metal which is quite improbable to be existing in such condition as,

 (3)

$$\underset{\text{Co-Co-Co}}{\overset{\text{C=O}}{|\;\;\;|}} \rightarrow \text{Co-}\overset{\substack{\text{C}\\ |}}{\text{Co}}\text{-}\overset{\substack{\text{O}\\ |}}{\text{Co}} \qquad (3)$$

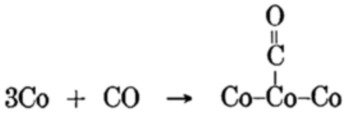
Furthermore,

$$M + H_2O \rightleftarrows MO + H_2 \qquad (4)$$

is a reversible process, and the reaction from right to left takes place more rapidly at lower temperatures (such as 190°–200°C.) ; the reverse process at higher temperatures. $CO+3Co=Co_2C+CoO$ cannot be obtained in the experimental conditions of ordinary Fischer synthesis. The heat of formation of links for CO is 235.5 Kcal. while those of Co_3–C and Co–O are 9.33 Kcal. and 57.5 Kcal., respectively, so that the heat of rupture for CO molecules is enormously large as compared to those of Co_3–C and Co–O; consequently, the reaction is very improbable from the energetic consideration.

A New Mechanism Proposed. We have proposed a probable mechanism (3) of Fischer–Tropsch synthesis reaction, which we shall now elucidate in a more detailed manner.

In the case of Co type catalyst, when a $(CO+2H_2)$ mixture is passed over the catalyst, after it is throughly reduced by H_2 stream, the reaction is

 (5)

$$3Co + CO \rightarrow \text{Co-}\overset{\substack{\text{O}\\ \|\\ \text{C}\\ |}}{\text{Co}}\text{-Co} \qquad (5)$$

(i.e. adsorbed state)

which in turn act as the active center of the said reaction; then

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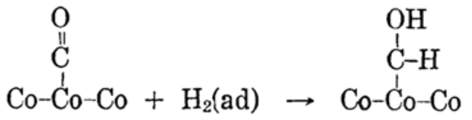
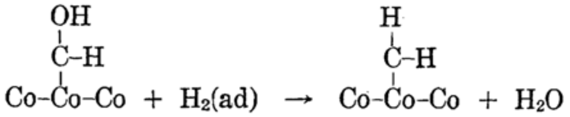
(4) (a) Ephraim, "Inorganic Chemistry", p 357.
(b) Watanabe, *Sci. Report Tohoku Imp. Univ.* Ser. I, **22** (1933), 892.
Reported the study of $CoO+CO \rightleftharpoons Co+CO_2$ of which the equilibrium is practically shifted to the CO_2 side even at 563°C. and it should be completly shifted to the CO_2 side at the temperature as low as 200°C. ;

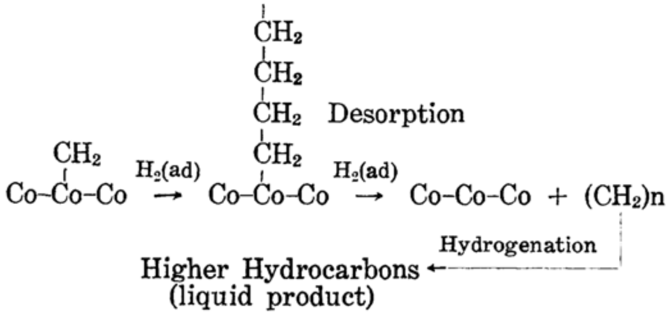
$\Delta F^\circ_{200} = -10344$ cal. $CO_2\% = 99.43\%$ at 563°C.
$CO_2\% = 95.87\%$ at 861°C.



$$\overset{\overset{\displaystyle O}{\|}}{\underset{|}{C}}\atop Co{-}Co{-}Co \;+\; H_2(ad) \;\rightarrow\; \overset{\overset{\displaystyle OH}{|}}{\underset{|}{C{-}H}}\atop Co{-}Co{-}Co \qquad (6)$$



$$\overset{\overset{\displaystyle OH}{|}}{\underset{|}{C{-}H}}\atop Co{-}Co{-}Co \;+\; H_2(ad) \;\rightarrow\; \overset{\overset{\displaystyle H}{|}}{\underset{|}{C{-}H}}\atop Co{-}Co{-}Co \;+\; H_2O \qquad (7)$$



$$\overset{CH_2}{Co{-}Co{-}Co} \xrightarrow{H_2(ad)} \overset{\overset{\overset{\overset{\overset{|}{CH_2}}{|}}{CH_2}}{\vdots}}{\overset{CH_2}{Co{-}Co{-}Co}} \xrightarrow[\text{Desorption}]{H_2(ad)} Co{-}Co{-}Co + (CH_2)n \qquad (8).$$

$$(CH_2)n \xrightarrow{\text{Hydrogenation}} \text{Higher Hydrocarbons (liquid product)}$$

Thus, CH_2 in adsorbed state polymerize to long chain hydrocarbons on the surface of catalyst; then the desorption in presence of H_2(ad) takes place; and finally with hydrogenation reaction, the observed liquid hydrocarbons are produced.

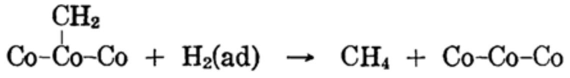
Table 1.

Temp. °C.	ΔF_t° cal./mol.	
25°C	−34547⁽⁵⁾	−34356⁽⁶⁾
100°	−30332	−30496
200°	−24712	−25123
300°	−19092	−19568
400°	−13472	−13890
500°	− 7852	− 8123

Discussion of the Mechanism. At the initial stage of the experiment, CH_4 formation predominates, this is probably due mainly to the following reaction,

$$CO + 3H_2 \rightleftarrows CH_4 + H_2O + 48.3 \text{ Kcal.} \qquad (9)^*$$

for which the free energy changes are tabulated in Table 1, but not through



$$\overset{CH_2}{Co{-}Co{-}Co} + H_2(ad) \rightarrow CH_4 + Co{-}Co{-}Co \qquad (10).$$

$\overset{CH_2}{Co{-}Co{-}Co}$ exists comparatively in a small amount as compared with that of H_2 in the beginning of the experiment, which shows that CH_4 formation predominates through reaction (9) rather than (10). More-

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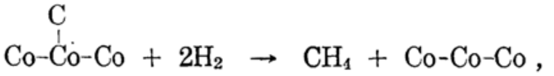
(5) C. Ellis, "The Chemistry of Petroleum Derivatives" Vol. II, (1937), 1225. (G. S. Parks and Huffman, "The Free Energies of Some organic Compounds", (1932).

(6) J. Chipman, *Ind. Eng. Chem.*, **24** (1932), 1013.

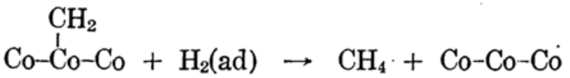
(*) The fact that if the ratio $CO : H_2 = 1 : 3$ or over, CH_4 formation is very active, indicates that this recation is very reasonable. (We also confirmed this fact (2b).)

over, the fact that CH_4 formation is mainly through (9) at the initial stage is quite clearly demonstrated in our experiment, i.e., when we pumped out completely the mixed gases after a regular synthesis, and only H_2 gas was passed at 200° C. (Reaction temperature), then we confirmed that there was no formation of CH_4, contrary to what had been claimed by Craxford$^{(2a)}$; but when a similar experiment was done at 300°C., we observed CH_4 formation as shown in Table 2 and Fig. 2. ($CO: H_2 = 1: 3.18$). According to the various "Carbide theory," it is explained that CH_4 formation in such a case is due to the following reaction.



$$\text{Co-}\overset{\text{C}}{\text{Co}}\text{-Co} + 2H_2 \rightarrow CH_4 + \text{Co-Co-Co}\,, \qquad (11)$$

but in our case, as there is definitely no CH_4, it is obviously explained as:



$$\text{Co-}\overset{CH_2}{\text{Co}}\text{-Co} + H_2(\text{ad}) \rightarrow CH_4 + \text{Co-Co-}\dot{\text{Co}} \qquad (12).$$

The reaction (12) is kinetically not observed at a temperature near 200°C., but at higher temperature (for example near 300°C.) it took place, as had been stated in our previous note$^{(3)}$. This is definitely confirmed as shown in Table 2 and Fig. 2.

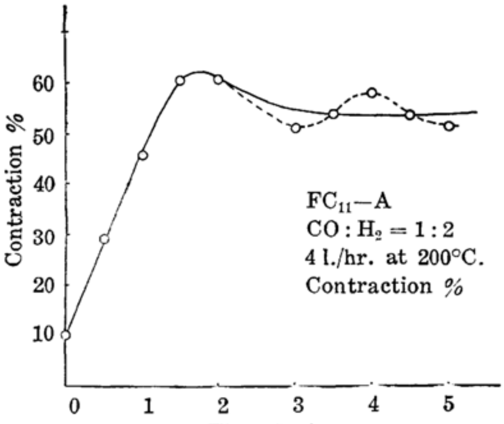


Fig. 1.

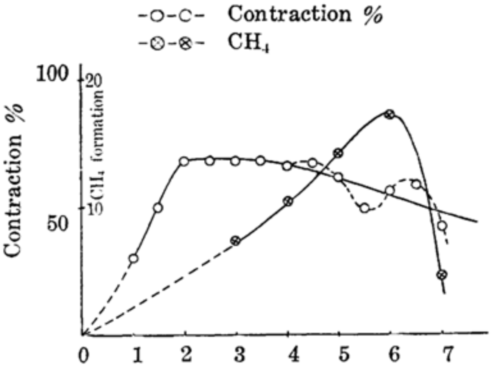


Fig. 2. FC_{11}—B $CO : H_2 = 1 : 318,4$ l./hr.
at 200°C
Oil yield 67.5 c.c./m^3

Furthermore, when we pretreated the catalyst with CO at 200°C. for 6–8 hours, and all the gases evacuated from the catalyst zone, and then only H_2 was passed, (4 l./hr.) in our desorption experiment, we observed that after certain period, CH_4 formation took place as shown in Fig. 3. (Of course, a certain time is spent for the gas to pass through the reaction vessel to the sampling part.) This time lag for CH_4 formation is probably due to the fact that CO must be desorbed before it reacts with H_2 as in Eq. (9); this in turn means that the reaction of CH_4 formation as in Eq. (9) is taking place in the gaseous phase and not on the

Table 2. Gas Analysis Data

After the regular synthesis, all the gas mixtures evacuated, and H_2 only was passed 4 l./hr. at 200°C. and 300°C.

Exp. No.	FC_{11}—A′(200°)	FC_{11}—B′(200°)	FC_{11}—I′(200°)	FC_{11}—N′(300°)
CO_2	0.2	0.2	0.2	0.1
C_2H_2	0.2	0.0	0.0	0.1
C_2H_4	0.2	0.0	0.0	0.0
CnH_{2n}	0.0	0.0	0.0	0.3
O_2	0.2	0.4	0.1	0.1
CO	0.7	0.2	0.6	0.3
H_2	96.8	96.9	96.4	93.1
CH_4	0.0	0.0	0.0	3.0
C_2H_6	0.0	0.0	0.0	0.5
N_2	1.7	2.3	2.7	2.5
Total	100.0	100.0	100.0	100.0

Table 3. Gas Analysis Data

The effect of CO : H_2 ratio on the CH_4 formation in the regular synthesis at 200°C. 4 l./hr.

Exp. No.	FC_{11}—A(CO : H_2 = 1 : 2) Contraction 59%	FC_{11}—B(CO : H_2 = 1 : 3.18) Contraction 68%
CO_2	1.8	3.8
C_2H_2	0.1	0.0
C_2H_4	0.1	0.0
CnH_{2n}	0.4	0.5
O_2	0.2	0.8
CO	29.6	5.6
H_2	56.2	58.1
CH_4	6.6(*)	17.1
C_2H_6	1.4	4.2
H_2	3.6	9.9
Total	100.0	100.0

catalyst surface. When H_2 streaming velocity was 8 l./hr. instead of 4 l./hr. and other conditions being the same, we observed that the above mentioned time lag for CH_4 formation was shortened, as expected. Hence, we may safely say that the reaction such as Eq. (9) is not occurring on the catalytic surface. A similar pretreatment was done with H_2 instead of CO, and CO only was passed after evacuation; then we found no CH_4 formation as shown in Fig. 4.

(*) CH_4 formation at the initial stage.

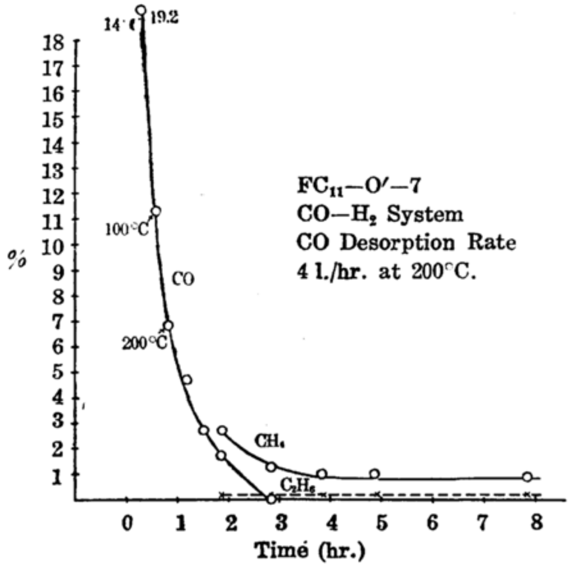


Fig. 3.

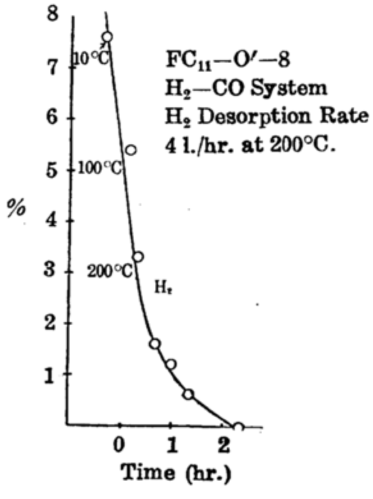
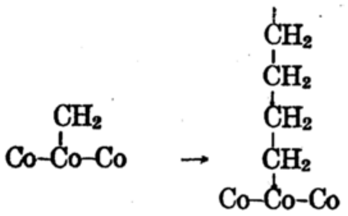


Fig. 4.

As time proceeds, the regular synthesis,



$$\text{Co-}\overset{\displaystyle CH_2}{\overset{|}{\text{Co}}}\text{-Co} \rightarrow \text{Co-}\overset{\displaystyle \overset{|}{CH_2}}{\overset{|}{\overset{\displaystyle CH_2}{\overset{|}{\overset{\displaystyle CH_2}{\overset{|}{\overset{\displaystyle CH_2}{\overset{|}{\text{Co}}}}}}}}}\text{-Co} \qquad (13),$$

gradually becomes vigorous in parallel with the increase of $\text{Co—}\overset{\displaystyle CH_2}{\overset{|}{\text{Co}}}\text{—Co}$. This is quite consistent with our observation that during certain initial period practically only H_2O and CH_4 formations were recognized and no liquid hydrocarbon was observed, but after certain period (at least 5–8 hrs.), the catalytic surface might possibly have rearranged in such a way as we had conceived in our mechanism, CH_2(ad) molecules gradually increased, and the desired liquid hydrocarbon was formed.

With regard to CH_2 of which carbon is said to be in divalent state⁽⁷⁾ and itself shows the nature of a molecule rather than a radcal, and a divalent carbon quite easily passes into a trivalent state. Some of its molecular characteristics are:

Life period	5.0×10^{-3} sec. (Thermal)
	6.4×10^{-3} sec. (Photochem.)

CH_2 "Bent molecule" for which the following constants are assigned:

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(7) R. F. Barrow, T. G. Person, and R. H. Purcell, *Trans Faraday Soc.*, **35** (1935), 880.

$$\nu(\sigma) = 3060 \text{ cm.}^{-1\,(8)}$$
$$\nu(\pi) = 3980 \text{ cm.}^{-1}$$
$$\delta(\pi) = 1450 \text{ cm.}^{-1}$$

The occurrence of CH_2 is without doubt as far as hydrocarbon chemistry is concerned as:

$$CH_2:CO + CH_2 \rightarrow C_2H_4 + CO \qquad (14)$$

(Olefin formation possible)

$$CH_4 \rightarrow CH_2 + H_2 \quad -47000 \text{ cal.}$$
$$E = 95 \text{ Kcal.} \qquad (15)$$

where E = activation energy,

if CH_2, then

$$CH_2 + CH_4 \rightarrow 2CH_3 \quad E = 12 \text{ Kcal.} \qquad (16)$$

$$CH_2 + CH_4 \rightarrow C_2H_6 + 36000 \text{ cal.,}$$
$$E = 44 \text{ Kcal.} \qquad (17)$$

$$C_2H_4 \rightarrow 2CH_2 \quad -53000 \text{ cal.} \qquad (18)$$
$$E = 77 \text{ Kcal. (Kassel)}^{(9)}$$
$$E = 150 \text{ Kcal. (Rice)}^{(10)}$$

$$CH_2 + C_2H_4 = C_3H_6 \qquad (19)$$

$$CH_2 + H_2 = CH_4 + 47000 \text{ cal.,} \qquad (20)$$
$$E = 32 \text{ Kcal.}^{(9)}$$

$$CH_2 \rightarrow CH + H, \quad 90 \text{ Kcal. endothermic,}$$
$$\therefore \text{ extremely stable} \qquad (21a)$$

$$2CH_2 \rightarrow C_2H_4 + 53000 \text{ cal.,} \qquad (21)$$
$$E = 24 \text{ Kcal.}^{(9)}$$

Voge(11) has calculated, from the Heitler-London-Pauling-Slater theory, the relative energies of formation of CH, CH_2, CH_3 and CH_4 as 4.0 e.v.

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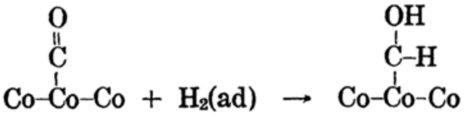
(8) Mecke, Leipziger Vorträge, (1931), 46.
R. F. Barrow, T. G. Person and R. H. Purcell, *Trans. Faraday Soc.*, **35** (1939), 880.

(9) L. Kassel, *J. Am. Chem. Soc.*, **54** (1932), 3949.

(10) F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals" (1935).

(11) (a) H. H. Voge, *J. Chem. Phys.*, **4** (1936), 581,
(b) G. Nordheim-Pöschl, *Ann. Physik*, **26** (1936), 258, 281 also gives estimates for the relative energies of CH_4, CH_3, CH_2 and CH based on the Heitler-London theory, and the results are in good agreement with those of H. H. Voge's calculation.

(92 Kcal.), 8.0 e.v. (184 Kcal.), 12.1 e.v. (279 Kcal.) and 17.0 e.v. (392 Kcal.) respectively. The value of 184 Kcal. for CH_2 is reasonable since it is practically twice the energy of C–H molecule (91 Kcal.) which is known from the spectroscopic data. The possibility that $CH_2+H_2 \rightarrow CH_4$ occurs at the surface of the vessel cannot be excluded at present; from the thermochemical evidence, the high reactivity with hydrogen is predictable. $CH_2+H_2 \rightarrow CH_4$ would be 80 Kcal.(*) exothermic whereas from Voge's data for CH_3 the alternative reaction, $CH_2+H_2 \rightarrow CH_3+H$, is 19 Kcal.(*) endothermic. The activation energy will be at least equal to the endothermicity and this is probably much greater than the activation energy of the highly exothermic reaction $CH_2+H_2 \rightarrow CH_4$ as pointed out by Bawn and Milsted;(11c) therefore $CH_2+H_2 \rightarrow CH_4$ is more probable, but as we already stated, during the normal synthesis, this reaction is found inhibited, i.e. CH_2(ad) interact much effectively with adjacent CH_2 (ad) as seen in Eqs. (20) and (21) through migration on the surface; concerning such possibility we will discuss a little later. Concerning the reaction (6)



$$\text{Co–}\overset{\overset{\text{O}}{\|}}{\overset{\text{C}}{|}}{\text{Co}}\text{–Co} + H_2(ad) \rightarrow \text{Co–}\overset{\overset{\text{OH}}{|}}{\overset{\text{C–H}}{|}}{\text{Co}}\text{–Co}$$

we can approximately estimate the activation energy, for we know that

Dissociation Energy(12)

$$\text{HCHO} \rightarrow \text{HCO} + \text{H} \qquad 85000 \text{ cal./mol.} \qquad (22)$$

$$\text{HCO} \rightarrow \text{CO} + \text{H} \qquad 19000 \quad ,, \qquad (23)$$

$$2\text{H} \rightarrow H_2 \qquad -103000^{(13)} \quad ,, \qquad (24)$$

by combining these (22), (23) and (24) we get

$$\text{HCHO} \rightarrow \text{CO} + H_2 \qquad 1000 \text{ cal.} \qquad (25).$$

Therefore

$$\text{CO} + H_2 \rightarrow \text{HCHO} \qquad -1000 \text{ cal.} \qquad (26)$$

Hence we can say that at least the activation energy for (26) is 1000 cal/mol; consequently if we consider HCHO is formed from the adsorbed CO and H_2 molecules the value of the activation barrier would be reduced to the extent of the respective heats of adsorption.

Furthermore, similarly we know that,

$$\text{HCHO} \rightarrow CH_2 + \text{O} \qquad 164000 \text{ cal./mol.}^{(12)} \qquad (27)$$

$$H_2O \rightarrow H_2 + \text{O} \qquad 115760 \quad ,, \qquad (28)$$

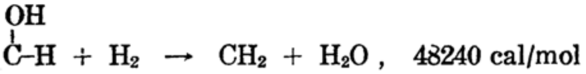
combining these (27) and (28) as before we get

(*) After correcting Voge's data for zero point energy.

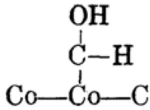
(11) (c) C. E. H. Bawn and J. Milsted, *Trans. Faraday Soc.*, **35** (1939), 889.

(12) H. Zeise, *Z. Elektrochem.*, **47** (1941), 238.

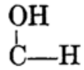
(13) Sidgwick, " Covalent Links in Chemistry " p. 119.



$$\overset{OH}{\underset{|}{C}}\text{-}H + H_2 \rightarrow CH_2 + H_2O\text{, } 48240 \text{ cal/mol} \qquad (29)$$

therefore at least the activation energy is 48240 cal./mol., so that if this type of reaction is proceeded through the molecules such as  $\begin{array}{c} OH \\ | \\ C\text{—}H \\ | \\ Co\text{—}Co\text{—}Co \end{array}$ and H_2(ad) the reaction rate would be much accelerated to the extent of the heats of adsorption since

$$k' = z_0 e^{-\frac{E-Q_1-Q_2}{kT}} \qquad \text{i.e.}$$

the activation energy will be lowered by the amount of Q_1 and Q_2 where Q_1 is the heat of adsorption of  $\overset{OH}{\underset{|}{C}}$—H on the catalyst surface and Q_2 is the heat of adsorption for H_2. Adopting the heat of adsorption for H_2 on Co practically the same as that of H_2 on Ni for which Beebe and Taylor⁽¹⁴⁾ have given (12600–14600), 48240 cal/mol will be reduced by at least 13000 cal./mol. which means E is about 35000 cal./mol. Of course, further reduction will be possible by the heat of adsorption for HCHO on Co for which at present the value is not known.

The rôle played by CH_2 during the normal synthesis of the Fischer-Tropsch reaction are no longer doubtful as it is evidenced by various accumulated facts in hydrocarbon chemistry in general⁽¹⁵⁾.

Starting from CH_2, if polymerized to C_2H_4, various reactions including polymerization and hydrogenation leading to higher hydrocarbons are quite easily attained as pointed out by Egloff, Schaad and Lowry⁽¹⁶⁾, furthermore, Egloff and Wilson⁽¹⁷⁾ pointed out that C_2H_4 acts as the key substance in hydrocarbon chemistry. Considering these, we have a very rational basis for our mechanism of the synthesis for which CH_2 plays the fundamental role in the formation of liquid hydrocarbons.

Egloff and Parrish⁽¹⁸⁾ stated that the activation energies of the polymerization reaction of the olefins are about 38—40 Kcal. This is much less than the energy required to break the bonds, hence the polymerization predominates at lower temperature for all the olefins.

The activation energies of some of the polymerization reactions are shown in Table 4.

In connection with the polymerization of the adsorbed CH_2 molecules on the catalyst surface, we must conceive that these molecules migrate freely to interact with each other, i.e.,

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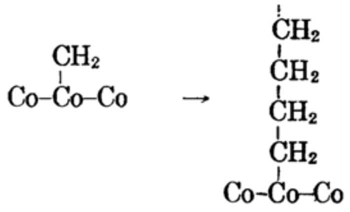
(14) Beebe and Taylor, *J. Am. Chem. Soc.*, **46** (1924), 43.
(15) (a) R. G. W. Norrish, *Proc. Roy. Soc.* (London) A, **150** (1925), 36.
 (b) L. S. Kassel, *J. Am. Chem. Soc.*, **54** (1932), 3949.
 (c) C. E. H. Bawn, *Trans. Faraday Soc.*, **34** (1938), 598.
 (d) E. W. R. Steacie, *Chem. Rev.*, **22** (1938), 311.
(16) Egloff, Schaad and Lowry, *J. Phys. Chem.*, **35** (1931), 1825.
(17) Egloff and Wilson, *Ind. Eng. Chem.*, **27** (1935), 917.
(18) Egloff and Parrish, *Chem. Rev.*, **19** (1936), 145.

Table 4. The Polymerization of the Olefins.(19)

Reactions	E cal./mol.
$2CH_2 \rightarrow C_2H_4$	24000(*)
$2C_2H_4 \rightarrow C_4H_8$	37700 (**)
$2C_3H_6 \rightarrow C\,H_{12}$	37400
$2C_4H_3 \rightarrow C_8H_{16}$	38000
2—iso $C_4H_8 \rightarrow C_8H_{16}$	43000
$2C_5H_{10} \rightarrow C_{10}H_{20}$	38000



the above reaction is controlled by the freedom of migration. Fortunately, there are very good evidences that under certain condition, the adsorbed molecules are capable of moving laterally over the surface. These are principally connected with the metal atoms and molecules of organic compounds, of these compound movement, for various reasons migrations are easier to follow but we can draw by analogy certain conclusions as to the probable behavior of the adsorbed gas molecules. Volmer(20) has shown that when mercury atoms are condensed from the vapor on a suitably cooled surface, the crystals which form grow nearly 1000 times as fast as in some direction as in others. This can only be due to the migration of the condensed atoms over the surface of the growing crystal until they reach the position of the maximum stability. Estermann(21) has found the similar evidence in case of cadmium condensed from the vapor, and for crystal growth of benzophenone by Adhikari(22). That Ba atoms can migrate in the same way over a tungsten surface has been demonstrated by Becker(23). This fact is beautifully shown by measuring the variation of thermoionic emission. Adsorbed Caesium(24) has also been shown to migrate in the same way. Thus in the mechanism which the author proposed, the way of migration of CH_2 on the catalytic surface cannot be far from these definite evidences.

With regard to adsorption, we must remember that while adsorption is necessary for catalytic action, the maximum adsorption does not necessarily coincide with the maximum catalytic activity(25), as often erroneously stated by some investigators. The amount of adsorption increases with the decrease of temperature; the rate of adsorption and the rate of chemical reaction both decreases; there is, however, an optimum temperature depending on these factors. Taylor and Burns(25b) have definitely demonstrated that the maximum catalytic activity does not occur at the temperature at which the maximum adsorption in their experiment of

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(*) Taken from L. Kassel (15b).

(**) $E = 38400$ and 38000, respectively, given in a later paper.
(Krauze, Nemtzov and Soskina, *J. Gen. Chem.* (U.S.S.R.), **5** (1935), 382.

(19) Tabulated in: F. W. R. Steacie, *Chem. Rev.*, **22** (1938), 311.

(20) Volmer, *Trans. Faraday Soc.*, **28** (1932), 359.

(21) Estermann, *Z. Elektrochem.*, **31** (1925), 441; *Z. Physik*, **33** (1925), 320.

(22) Adhikari, *Z. Physik.*, **35** (1925) 170.

(23) Becker, *Trans. Faraday Soc.*, **28** (1932), 148.

(24) Taylor and Langmuir, *Phys. Rev.*, **44** (1933), 423.

(25) (a) Smithells, "Gases and Metals", (1938), p. 69.
(b) H. S. Taylor and R. M. Burns, *J. Am. Chem. Soc.*, **43** (1921), 1273.

hydrogenation of ethylene, and similar observations may be made with respect to a cobalt catalyst with carbon monoxide and hydrogen, and with nickel in the case of carbon dioxide and hydrogen. Considering these, again, we may say that Kodama's interpretation with regard to this phenomenon, i.e., the necessary coincidence of maximum catalytic activity and maximum adsorption is quite improbable (if there is, a happy coincidence). Of course, the magnitude of the heat of adsorption is definitely related to the catalytic activity by the relation already stated.

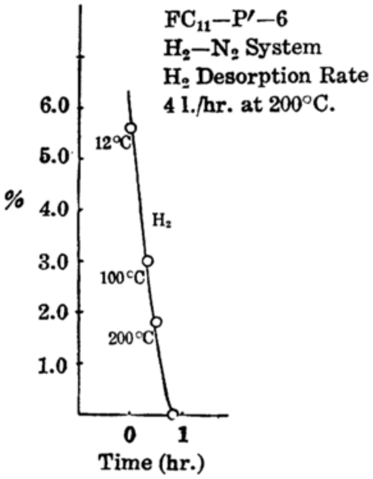


Fig. 5.

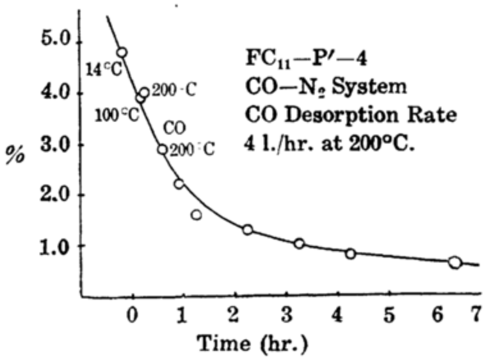


Fig. 6.

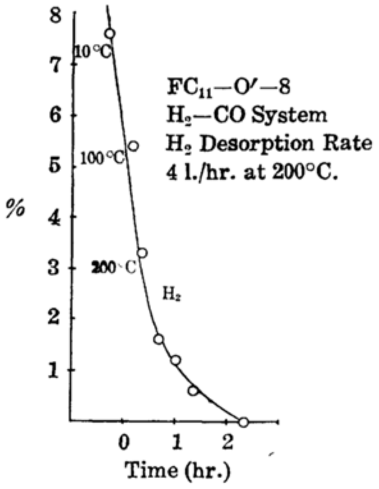


Fig. 7.

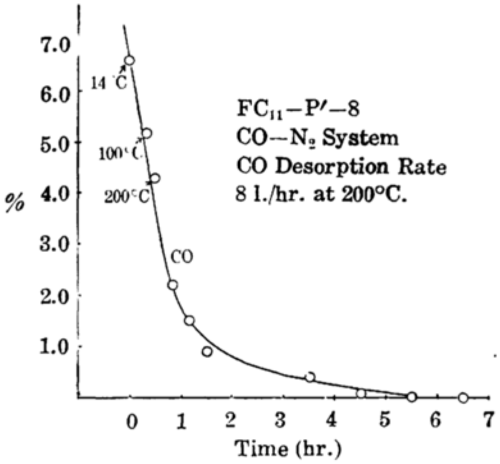
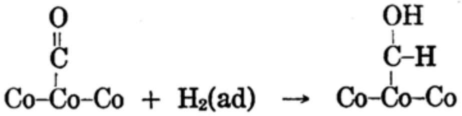


Fig. 8.

Furthermore, Taylor has demonstrated that carbon monoxide is very firmly adsorbed by metals and that at moderate partial pressure, it probably covers the metal surface completely. Thus, in such a case, H_2 in the presence of CO can be adsorbed only on the surface of carbon monoxide and not on the metal surface.

With regard to this point that carbon monoxide is more firmly adsorbed on the surface of the catalyst has also been demonstrated in our desorption experiments of CO, H_2 and N_2 from the catalysts. The details of the experiments will be published in our subsequent paper. Figs. 5—8 show some of the adsorptive characteristics for H_2 and CO at 200°C.. The point that H_2 in the presence of CO can be adsorbed only on the surface of CO and not on the metal may be conceivable and furthermore, it is quite concordant with our mechanism, that is, in the Fischer–Tropsch reaction. When the catalyst at first is reduced by streaming H_2, such reduced catalyst is covered by adsorbed hydrogen. At the beginning, as a $(CO+2H_2)$ mixture is passed, since CO is more strongly and easily adsorbed than H_2, it is quite reasonable to assume that some of the already adsorbed hydrogen is replaced by CO and some hydrogen remains, and the replaced hydrogen may immediately be attached to CO(ad), as shown in our mechanism, i.e., through the migration of the adsorbed molecule



$$\mathrm{Co{-}\overset{\substack{O\\ \|\\ C\\ |}}{Co}{-}Co + H_2(ad) \rightarrow Co{-}\overset{\substack{OH\\ |\\ C{-}H\\ |}}{Co}{-}Co}$$

This is quite reasonable from our approximate values of its activation energy which is 1000 cal./mol.(*); hence the above reaction is quite rapid. This value may correspond to the potential barrier for the process of surface migration(26).

J. K. Roberts(27) has also demonstrated that in his experiment of the adsorption of oxygen on a tungsten surface already covered with H_2, when an oxygen molecule is adsorbed, a hydrogen molecule is thrown off; every oxygen molecule adsorbed throws off a molecule of H_2. Moreover, he concluded that the hydrogen must be thrown off as molecule, not as separate atoms from his direct measurement of the heat of adsorption.

Considering the surface partially covered by oxygen, it is stated that the activated adsorption of hydrogen is connected with the interaction between hydrogen (thrown off hydrogen) and surface oxygen in the adsorbed state or that forming a integral part of the solid lattice.

This is quite analogous to our case of H_2 covered catalyst surface, once, it is partially replaced by CO and the fraction of H_2 is thrown off by CO, and immediately, through the surface migration, H_2 interacts with the adsorbed CO as shown in our theory.

Thus by applying our proposed mechanism to the Fischer-Tropsch reaction, all the facts of experimental observations are practically explained quite satisfactorily.

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(26) Lennard-Jones, *Trans. Faraday Soc.*, **28** (1932), 333. From the point of view of wave mechanics the question of surface migration has been considered by: Lennard-Jones and Strachan, *Proc. Roy. Soc.* (London), A **150** (1935), 442.

(27) J. K. Roberts, *Proc. Roy. Soc.* (London), A **152** (1935), 477.

(*) E. K. Rideal, *Trans. Faraday Soc.*, **28** (1932), 139, cites $E = 1000$ cal./mol. for the potential barrier for the process of surface migration in H_2 adsorbed on Ni from the experiment of Davisson and Germer, *Phys. Rev.* **2** (1927), 35, 705.

If the catalyst is of Fe type, our mechanism is equally satisfactory; the reactions (5) (6) (7) and (8) should proceed equally as well and in the presence of Fe catalyst, H_2O produced reacts as

$$CO + H_2O \rightleftarrows H_2 + CO_2 + 10.6\,\text{Kcal.} \qquad (30).$$

This reaction is quite fast over the Fe catalyst. The equilibrium is quite shifted to the CO_2 side as shown in the values of ΔF°.

Table 5.

Temp. °C.	ΔF° cal./mol.	
25°	−7241(28)	−6810(29)
100°	−6484	−6057
200°	−5494	−5115
300°	−4536	−4209
400°	−3611	−3340
500°	−2721	−2500

As observed experimentally, no H_2O formation but only CO_2, (of course, even in the case of Co and Ni type catalyst this water gas reaction is occurring) hence we observe a very slight amount of CO_2 formation as seen in the gas analysis data.

However, in the case of Fe catalyst usually the experiment is proceeded at above 250°C., and in such experimental conditions the reaction is quite rapid. If this is carried on at near 200°C., even in the Fe type catalyst, we have observed the formation of H_2O. This is quite obviously due to the fact that the H_2O formed during the synthesis is not used up rapidly enough in the water gas reaction to give CO_2, so that the CO_2 formation in the Fe catalyst is considered as secondary.

Table 6. Gas Analysis Data.

Types of catalyst	Co Type		Fe Type		(Co+Fe) Type	
Exp. No.	F_{45}—H	F_{45}—B(*)	F_{28}—A	F_{57}—C	F_{53}—D	F_{54}—C
CO_2	0.6	12.4	20.4	3.8	1.9	1.0
C_2H_2	0.0	0.0	0.0	0.0	0.0	0.2
C_2H_4	0.4	0.3	0.8	0.2	0.2	0.0
CnH_{2n}	0.0	0.0	0.5	0.2	0.0	0.0
O_2	0.5	1.5	0.3	0.5	0.1	0.2
CO	30.5	1.6	26.2	45.2	33.1	30.0
H_2	63.9	30.1	50.3	46.6	60.0	65.5
CH_4	0.0	45.8	0.0	0.0	0.0	0.0
C_2H_6	0.0	0.0	0.0	0.0	0.0	0.0
N_2	4.1	8.3	1.5	3.5	4.7	3.1
Total	100 0	100.0	100.0	100.0	100.0	100.0

In the case of (Co+Fe) type catalyst, in which the experiment proceeded at 200°C., we demonstrated that the formation of H_2O is the same as in the case of Co catalyst.

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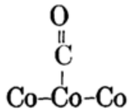
(28) Lewis and Randall, "Thermodynamics", (1923) 575.

(29) J. Chipman, *Ind. Eng. Chem.*, **24** (1932), 1013.

(*) Initial stage of the reaction where CH_4 formation is predominating.

Thus we can safely say that our proposed mechanism explains very concordantly the experimental observations not only for Co and Ni type catalysts but also for Fe type catalyst for which, so far, it has been considered that an entirely different mechanism should play.

The inhibitive action of CO on the occlusive power of palladium for hydrogen was recognized by von Hemptinne.(30) This is similar to our results in that, when CO pretreatment at 350°C. was done for the catalyst, it destroyed the activity, i.e., when the CO treatment is made, the entire surface is covered by CO which may prevent the adsorption of H_2. This is necessary for obtaining the activated hydrogen which reacts with the adsorbed



$$\overset{\overset{\displaystyle O}{\|}}{\underset{\displaystyle \text{Co–}\overset{|}{\text{Co}}\text{–Co}}{C}}$$

to give CH_2 molecule (ad) for the regular synthesis of CH_2 (ad) → polymerization → desorption → hydrogenation → higher hydrocarbon. The Pd case seemed to be applicable also in the case of Co surface in the Fischer synthesis. This fact is very concordant with that when CO is used in the reduction of the catalyst at 350°C. instead of H_2 for the preparation of the catalyst, it does not show as good catalytic activity as when H_2 is used in the reduction. However, after the catalyst is being normally reduced by H_2 and then CO pretreatment was done at the temperature of reaction (190°–200°C.), then the activity is quite as good.

This is clearly shown in our experiment.

Table 7.

Various pretreatments for Co catalyst (XII_{16}—1)

Subs.	Temp. °C.	React. Temp.	Activity	Exp. No.	Contraction (%)
CO	350°	200°	Activity destroyed. No oil formation.	FC_{11}—C	13
CO	200°	200°	Good.	FC_{11}—D FC_{11}—L FC_{11}—M	14 30 34
N_2	200°	200°	Not so good.	FC_{11}—J FC_{11}—H	28 31
H_2	200°	200°	Good.	FC_{11}—I	40
H_2	350°	200°	Not so good as at 200°C. with respect to its oil formation.	FC_{11}—F	21

The explanation for this is very clear as already discussed in connection with Roberts' experimental evidence and our desorption experiments.

The experimental data for the series of this investigation will be given in our subsequent papers to be published elsewhere.

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(30) von Hemptinne, *Z. phys. Chem.*, **27** (1898), 429.

Summary.

(1) Introductory remarks for the Fischer-Tropsch reaction in connection with various mechanisms so far proposed are presented briefly.

(2) Our proposed mechanism is presented and discussed in detail.

(3) The role of CH_2 in hydrocarbon chemistry in general is stressed especially in connection with the Fischer-Tropsch reaction mechanism.

(4) Approximate values of the activation energies for the reactions involved in the synthesis are presented and discussed in correlation with adsorption.

(5) The aspect of polymerization process is discussed, and the question of surface migration is correlated with the polymerization reaction.

(6) Adsorption and catalytic activity involved in the synthesis are discussed in the light of our desorption experiment.

(7) The proposed mechanism is also applied to Fe type catalyst and discussed.

(8) Various pretreatment effects on the catalytic activity are discussed in the light of our experimental evidences.

In conclusion, the author expresses his hearty thanks to Dr. T. Marusawa, Former Director of the Institute, and Dr. S. Sato, Director of the Institute, for their interests and constant encouragement for carrying on this investigation and for the permission for this publication. Also the author takes this occasion to extend his thanks to Dr. R. Negishi who willingly has criticized and discussed the problem throughout this investigation—also to his colleagues; and to Messrs. S. Hayashi, Shimamura, Igarashi, Fujiwara and Kuwabara who were willing to assist in our experimental part of this investigation; and to Messrs. Kataoka, Inaba, Kodama and Nakano who have helped with their part in the analytic work.

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