

338. *The Mechanism of the Synthesis of Hydrocarbons from Water Gas.*

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Experiments on the rates of formation and reduction of cobalt carbide on cobalt-thoria-kieselguhr catalysts under various conditions indicate that the first step in the Fischer-Tropsch synthesis of hydrocarbons from carbon monoxide and hydrogen is the reaction of these gases with the catalyst to give cobalt carbide. When this is reduced by chemisorbed hydrogen atoms, as indicated by the ortho-para-hydrogen conversion, methane only is formed, and no higher hydrocarbons. Reduction by molecular hydrogen—absence of ortho-para-conversion—leads to formation of oils. Hence, in order to obtain oils, the conditions of the synthesis have to be adjusted so that only very few chemisorbed hydrogen atoms are present on the catalyst surface, and then, not only are the ortho-para-hydrogen conversion and the synthesis of methane inhibited, but also the water-gas shift reaction, and the catalytic hydrogenation-cracking of paraffin hydrocarbons.

FISCHER and TROPSCH (*Ber.*, 1926, **59**, 830) noted that, on passage of a mixture of carbon monoxide and hydrogen over an iron or cobalt catalyst maintained at 200–250°, long-chain paraffins and olefins were produced. The present investigation was carried out to elucidate the mechanism of this reaction, which possesses the following interesting characteristics. One of the best catalysts now used is of the type developed by Fischer and Koch (*Brennstoff. Chem.*, 1932, **13**, 61), and contains cobalt, thoria, and kieselguhr in the proportions 100 : 18 : 100. It is prepared by precipitation as carbonates and reduction with hydrogen at 375°. When this freshly reduced catalyst is maintained in contact with synthesis gas, $\text{CO} + 2\text{H}_2$, at 195°, methane, carbon dioxide, and some water are formed, but if the temperature is 150° at the beginning and is raised very slowly to 195°, methane and carbon dioxide are formed at first as before, but the Fischer synthesis of oils and water gradually sets in and replaces the synthesis of methane and carbon dioxide (Herington and Woodward, *Trans. Faraday Soc.*, 1939, **35**, 958). The Fischer synthesis is restricted to a narrow temperature range, oil being scarcely formed at all below 175°,

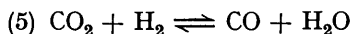
and being replaced by methane and carbon dioxide above 225° (Tsuneoka and Murata, *J. Soc. Chem. Ind. Japan*, Suppl. 1937, **40**, 478B). The synthesis of methane persists at very much higher temperatures, *e.g.*, 370°. After continued synthesis of oil, the catalyst gradually loses its activity but can be revived almost completely by treatment with hydrogen at the synthesis temperature. When this hydrogen is replaced by synthesis gas, the revived catalyst forms carbon dioxide and methane for the first few hours, and then normal synthesis sets in, thus exhibiting a striking contrast to the behaviour of a freshly reduced catalyst (Herington and Woodward, *loc. cit.*). Finally, pressures of 50 atm. or more induce the formation of oxy-compounds such as alcohols, acids, and aldehydes (Fischer and Küster, *Brennstoff. Chem.*, 1933, **14**, 3).

It is significant that the three metals, cobalt, nickel, and iron, which show activity as Fischer catalysts at atmospheric pressure, all react at 200° with carbon monoxide to form carbides, and Fischer has always postulated that such carbides are intermediate compounds in the synthesis. Bahr and Jessen (*Ber.*, 1930, **63**, 2227) found that precipitated and reduced cobalt reacted smoothly at 230° with carbon monoxide as follows: $2\text{CO} + 2\text{Co} \longrightarrow \text{Co}_2\text{C} + \text{CO}_2$. At higher temperatures the carbide becomes unstable and free carbon is formed as well. On conversion into carbide, cubic nickel passes over into metal of hexagonal symmetry (Jacobson and Westgren, *Z. physikal. Chem.*, 1933, *B*, **20**, 361).^{*} When reduced by solution in dilute acids, these carbides give hydrocarbons higher than methane, iron carbide, *e.g.*, giving gaseous, liquid, and solid hydrocarbons. Cobalt carbide can also be reduced readily by hydrogen at 250°. There is good experimental evidence for the assumption that carbide accumulates on the catalyst during the Fischer synthesis. If an active used catalyst is treated with hydrogen at 200°, large quantities of methane are obtained. Göthel ("Grenzflächen-Katalyse," Hirzel, Leipzig, 1933, p. 67) found that the electrical conductivity of the powdered catalyst varied during synthesis in such a way as to indicate the progressive formation of carbide. Le Clerc and Lefebure's X-ray results (*loc. cit.*) really show the same thing, although they interpret them differently. Finally, a number of carbon balances for the synthesis, and analysis of the products of decomposition of used catalysts with hydrochloric acid carried out by Fischer and Tropsch (*Ges. Abh. Kenntn. Kohle*, 1930, **10**, 313), showed that carbide was built up during the synthesis.

The Reactions of Carbon Monoxide and Hydrogen with the Fischer Catalyst.—During the synthesis, the catalyst is in contact with both hydrogen and carbon monoxide, and the formation and utilisation of the carbide can be envisaged as follows:

- (1) $\text{Co} + \text{CO} \longrightarrow \text{Co-CO}$ (chemisorption)
- (2) $\text{Co-CO} + \text{CO} \longrightarrow \text{Co-C}$ (surface carbide) + CO_2
- (3) $\text{Co-CO} + \text{H}_2 \longrightarrow \text{Co-C}$ (surface carbide) + H_2O
- (4) $\text{Co-C} + \text{H}_2 \longrightarrow \text{CH}_4 \longrightarrow$ higher hydrocarbons

The oxygenated product of the Fischer synthesis is water and not carbon dioxide, a fact which suggests that (3) proceeds more rapidly than (2), for it is impossible that the water could be produced by the water-gas shift reaction



since at 200° the equilibrium concentration of water vapour would be extremely small. Indeed, it is clear 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. It thus seems likely that the first stage in the Fischer synthesis is the reaction of adsorbed carbon monoxide with hydrogen to give carbide and water. To confirm this point a series of experiments were carried out with an active Fischer catalyst containing cobalt, thoria, and kieselguhr in the proportions 100 : 18 : 100, prepared by the method described in the Annual Reports of the Fuel Research Board (1938, p. 189).

^{*} In view of the evidence adduced by Bahr and Jacobson and their colleagues (*loc. cit.*), Le Clerc and Lefebure (*Compt. rend.*, 1939, **208**, 1583, 1650) appear to be in error in assuming that this hexagonal substance is an allotrope of nickel, for it is clearly Ni_3C .

When carbon monoxide is put in contact with freshly reduced Fischer catalyst at 150–250°, and carbide formation occurs by reactions (1) and (2), there is at first a relatively rapid reaction, which is followed, after the first few hours, by a slow second stage independent of the pressure when this is above 30 cm. These reactions are shown in Figs. 1, 2, and 3. Their apparent activation energies are 10,000 and 18,000 cal. respectively (see Fig. 4). If at any time during the second slow stage the reaction gases are pumped off and fresh carbon monoxide is introduced, the initial rapid reaction is not

FIG. 1.

Rate of the initial fast stage of the reaction
 $2\text{Co} + 2\text{CO} \rightarrow \text{Co}_2\text{C} + \text{CO}_2$.

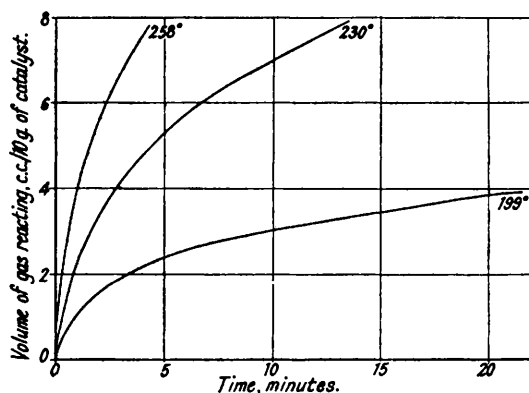


FIG. 2.

Rate of the second stage of the reaction $2\text{Co} + 2\text{CO} \rightarrow \text{Co}_2\text{C} + \text{C} + \text{CO}_2$ on the Fischer catalyst.

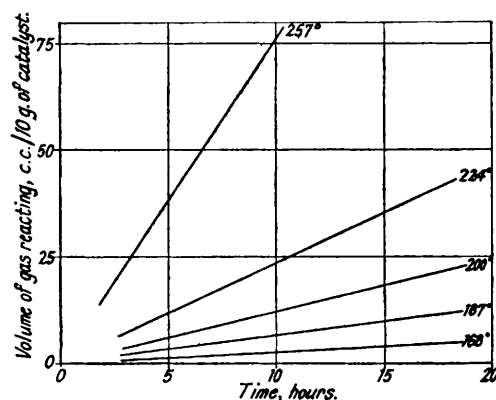


FIG. 3.

Dependence of the second stage of the reaction $2\text{Co} + 2\text{CO} \rightarrow \text{Co}_2\text{C} + \text{CO}_2$ on pressure at 200° for the Fischer catalyst.

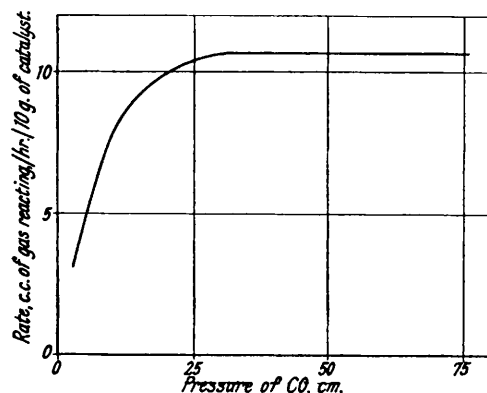
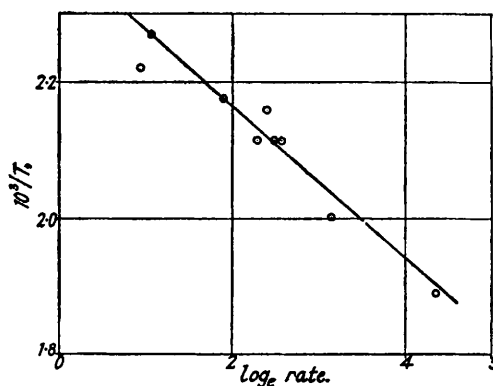


FIG. 4.

The energy of activation of the second stage of the reaction $2\text{Co} + 2\text{CO} \rightarrow \text{Co}_2\text{C} + \text{CO}_2$ for the Fischer catalyst.



observed, and this suggests that the rapid reaction is that occurring on the active parts of the catalyst surface, whereas the slow stage is the formation of carbide in the bulk of the metal. This would account satisfactorily for the difference in the activation energies, because it is known that the formation of carbide in bulk requires an alteration in the crystal structure of the metal (Jacobson and Westgren, *loc. cit.*). It should be mentioned that the fast initial reaction cannot be explained in the more obvious way as the reaction of carbon monoxide with hydrogen which has remained chemisorbed on the catalyst after the reduction, because such reactions are very much faster indeed than the present initial stage of carbide formation.

The rate of reduction of the carbide by hydrogen is given in Fig. 5, and Fig. 6 gives

the apparent energy of activation of the reaction as 11,500 cal. Normally the reaction proceeds as $\text{Co}_2\text{C} + 2\text{H}_2 \rightarrow 2\text{Co} + \text{CH}_4$, but at very low temperatures, *e.g.*, 140° , the hydrocarbon gas formed (represented as $\text{C}_n\text{H}_{2n+2}$) had an n value of 1.12, showing that a small but definite amount of higher hydrocarbons was being formed in addition to the methane. Comparison of Figs. 2 and 5 shows that the reduction of the carbide is a much

FIG. 5.

Rates of the reaction $\text{Co}_2\text{C} + 2\text{H}_2 \rightarrow \text{CH}_4 + 2\text{Co}$ on the Fischer catalyst.

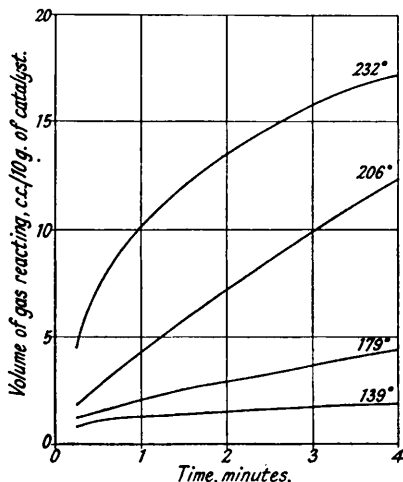


FIG. 6.

Energy of the activation of the reaction $\text{Co}_2\text{C} + 2\text{H}_2 \rightarrow \text{CH}_4 + 2\text{Co}$ on the Fischer catalyst.

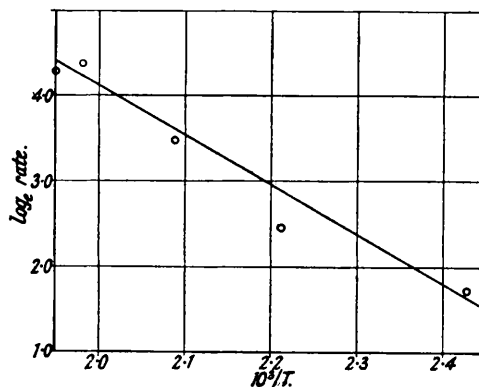


FIG. 7.

Rates of the reaction $2\text{H}_2 + \text{CO} \rightarrow$ on the Fischer catalyst.

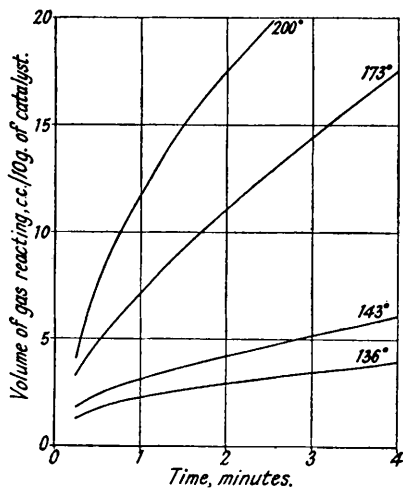
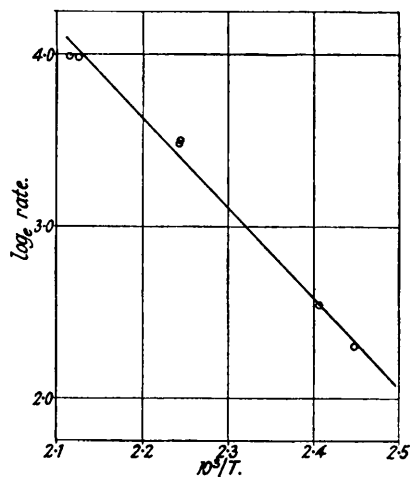


FIG. 8.

Energy of activation of the reaction $\text{CO} + 2\text{H}_2 \rightarrow$ on the Fischer catalyst.



more rapid reaction than its formation by reaction (2), and hence that carbide cannot accumulate on a catalyst in contact with carbon monoxide and hydrogen if it is being formed only by reaction (2). Since carbide does accumulate on the Fischer catalyst during synthesis, however, it must be formed by some reaction faster than its reduction, and the only possibility is reaction (3), where chemisorbed carbon monoxide is reduced to carbide by hydrogen. Although this reaction cannot be isolated, its rate will be at least as great as, and possibly greater than, that of the total reaction of $2\text{H}_2 + \text{CO}$ on the

catalyst, if it be granted that it occurs as a step in the total reaction. The curves giving the rates and the apparent energy of activation of 9,500 of the total reaction are in Figs. 7 and 8. (All the activation-energy data given here appear to be reasonably accurate, because not only was the activity of the catalyst found to suffer no appreciable decay during each series of measurements, but the data were also reproducible with different samples of the same batch of catalyst.) In accordance with the items expressed above,

FIG. 9.
Dependence of the reaction $\text{CO} + 2\text{H}_2$ on the composition of the gas.

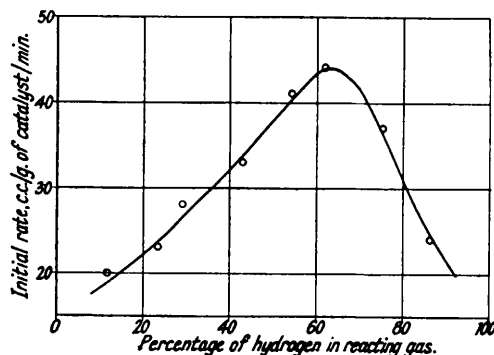
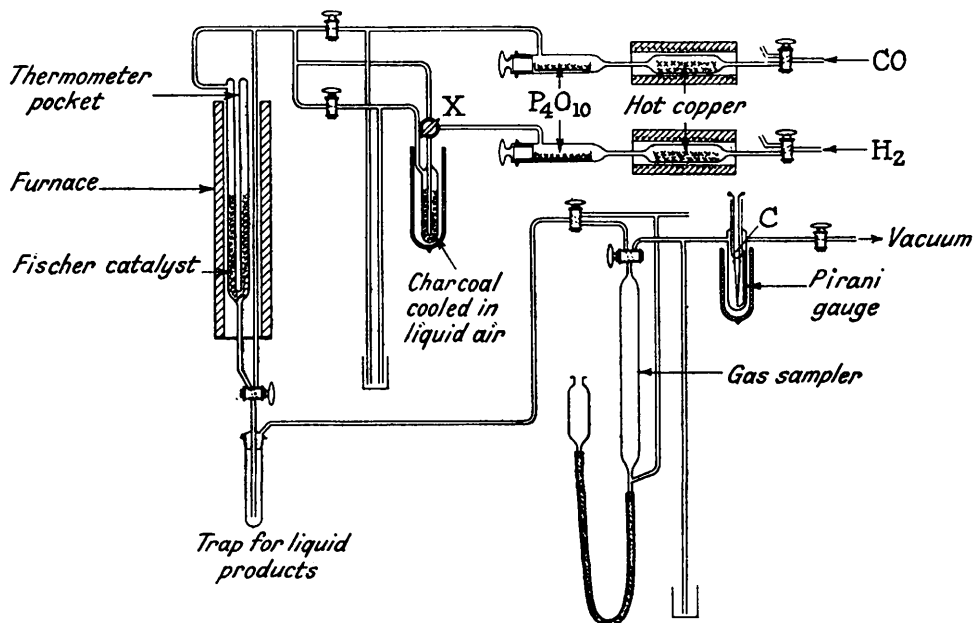


FIG. 10.

Apparatus for the Fischer synthesis with ortho- or para-hydrogen.



the formation of carbide by the reactions (1) and (3) is faster than the reduction of the carbide, and thus the accumulation of carbide during the Fischer synthesis is explained. Fig. 9 shows the dependence of this reaction on the composition of the gases, the total initial pressure being 1 atm., and the temperature 178°, and the fact that this curve has its maximum near the composition $\text{CO} + 2\text{H}_2$ show that initially, at any rate, the hydrogen and the carbon monoxide are competing on more or less equal terms for the catalyst surface and neither the one nor the other monopolises it during the beginning of

the reaction. The next stage of the Fischer synthesis is the reduction of the carbide so formed to give higher hydrocarbons, or to give methane.

The ortho-para-Hydrogen Conversion in Synthesis Gas.—Although the exact mechanism of the ortho-para-hydrogen conversion is still a matter of dispute, it is generally agreed that, when the conversion is proceeding on a metal surface, chemisorbed hydrogen atoms are present on it, and that the conversion may thus be taken as a means of detecting the presence of chemisorbed hydrogen atoms. It seemed important to investigate whether the syntheses of higher hydrocarbons and of methane could be differentiated in this manner. The experimental arrangements shown in Fig. 10 allowed synthesis gas composed of carbon monoxide and para-hydrogen, or of carbon monoxide and normal equilibrium hydrogen, to be passed alternately over the catalyst and allowed the gaseous products to be analysed in a thermal conductivity gauge after freezing out the condensable fractions. Then, from the experimental data on the conductivities of the two gaseous mixtures the extent of the conversion of para- into ortho-hydrogen in the first mixture could be determined. Although the presence of a variable residual amount of carbon monoxide and of methane greatly lowered the efficiency of the gauge, the extent of conversion could readily be ascertained to within $\pm 5\%$. The experimental data are cited in the Table, and the results may be summarised as follows. While the Fischer synthesis is proceeding at about 200° the ortho-para-conversion does not occur to any marked extent; but it does occur for all the following conditions under which either there is no reaction or else methane is being formed.

(i) With normal synthesis gas, $\text{CO} + 2\text{H}_2$, at temperatures below 140° , in which case there is no reaction.

(ii) With synthesis gas at 200° for the first hour or so of the reaction, during which time methane and cobalt carbide are being produced and no oil.

(iii) With a mixture of $24\text{H}_2 + \text{CO}$ at 200° even after 24 hours. With this gas mixture hardly any oil is formed, only methane.

(iv) With synthesis gas above 250° . Again, methane is the product and no oil.

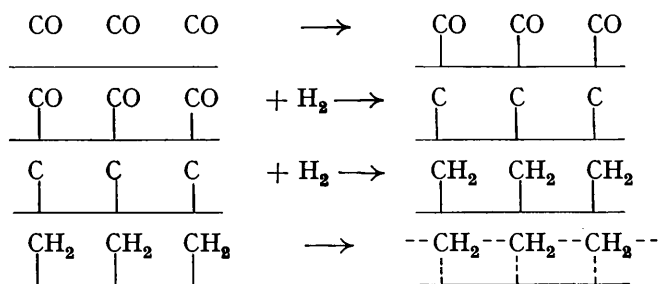
The conclusion to be drawn from these results is that when oil is being formed there

Catalyst.	Gas.	Temp.	Time from start, hrs.	Gas rate, l./hr.	Conversion of $p\text{-H}_2$, %.	Reaction products.
None	H_2	200°	—	—	0	
Active catalyst	H_2	200	—	—	100	
" "	$\text{CO} + 5.8\text{H}_2$	200	0.5	5.0	>95	CH_4 , no oil
" "	"	200	1.0	5.0	42	CH_4 and oil
" "	"	200	4.5	5.0	< 5	Oil; very little CH_4
" "	$\text{CO} + 14\text{H}_2$	200	0.25	5.0	>95	CH_4 only
" "	"	200	1.0	5.0	66	CH_4 and a little oil
" "	$\text{CO} + 24\text{H}_2$	200	0.25	3.6	>95	CH_4 only
" "	"	200	3.0	3.6	60	CH_4 and a little oil
" "	$\text{CO} + \text{H}_2$	128	5.0	2.9	>95	No reaction
" "	$\text{CO} + 5\text{H}_2$	125	5.0	6.0	>95	No reaction
" "	"	145	5.0	6.0	>95	No reaction
" "	$\text{CO} + 2.75\text{H}_2$	145	5.0	3.8	>95	No reaction
" "	"	160	3.0	3.8	75	CH_4 and a little oil
" "	$\text{CO} + 1.5\text{H}_2$	175	6.0	2.6	75	CH_4 and a little oil
" "	$\text{CO} + 2\text{H}_2$	175	24.0	3.1	75	CH_4 and a little oil
" "	"	200	4.0	10.0	70	Oil. For this experiment a very short catalyst bed and a high rate of flow were used
" "	"	200	4.0	4.0	40	Oil. A very long catalyst bed was used, and the result shows that the latter part of the bed, which is not actively engaged in the synthesis, is not freely active for the $o\text{-}p$ conversion
" "	"	250	4.0	4.0	78	Very little oil, much methane and gas. Molecular ratio of $\text{H}_2\text{O}/\text{CO}_2$ is 8.25. If the water-gas shift and the $o\text{-}p$ conversion inhibitions were running strictly parallel, the $\text{H}_2\text{O}/\text{CO}_2$ ratio would have been 22:78, <i>i.e.</i> , 0.3
" "	$\text{CO} + 2.4\text{H}_2$	300	4.0	5.3	90	CH_4 , a little gas, no oil
Active catalyst carbided for 18 hours at 200°	H_2	25	4.0	4.0	<5	
" "	H_2	200	0.3	4.0	92	The carbide is rapidly reduced at 200° .
Active catalyst poisoned by sulphur at 300° so as to be entirely inactive for the Fischer synthesis at 200°	H_2	18	4.0	4.0	0	
" " " "	$\text{CO} + 4\text{H}_2$	200	4.0	4.0	86	No reaction
" " " "	"	320	4.0	4.0	79	Rapid reaction to give CH_4
Blue cobalt catalyst from another source	H_2	200	4.0	4.0	>95	No reaction
" " " "	$\text{CO} + 2\text{H}_2$	210	4.0	4.0	>95	No reaction
" " " "	"	286	4.0	4.0	5	Oil, gas, and methane

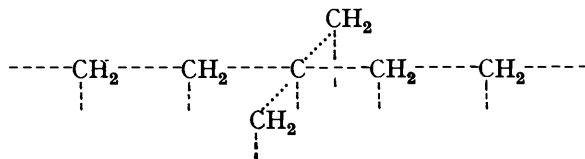
is no appreciable conversion, and hence no appreciable amount of chemisorbed hydrogen is present on the catalyst. The synthesis of oil thus proceeds by way of molecular hydrogen. On the other hand, methane synthesis involves at some stage the presence of chemisorbed hydrogen. These conclusions are confirmed by the results obtained for the two abnormal catalysts given at the foot of the Table. One is a catalyst poisoned by sulphur so as to make it inactive for the synthesis of oil, but which still forms methane rapidly at 300°; at this temperature it also catalyses the ortho-para-hydrogen conversion actively. The other is a cobalt catalyst which still remained incompletely reduced after prolonged treatment with hydrogen at 375°, and gave no Fischer reaction at 200° but began to form higher hydrocarbons at 280°, at which point the ortho-para-conversion begins to fall off.

The inhibition of the conversion during the synthesis of oils may be due either to the surface being completely covered with carbide, since carbide does stop the conversion (Table I), or to the presence of chemisorbed hydrocarbons, for, although the saturated hydrocarbons do not inhibit the conversion, yet Farkas, Farkas, and Rideal (*Proc. Roy. Soc.*, 1934, **146**, 630) found that ethylene, which is very strongly chemisorbed, does so. In either case it is clear that when cobalt carbide on the catalyst is attacked by molecular hydrogen higher hydrocarbons are formed, but if chemisorbed hydrogen is present the reduction process goes further and methane is produced. Some insight into the mechanism of the formation, growth, and final desorption of the hydrocarbons can be obtained in the light of this result and the following considerations.

The Hydrogenation-cracking of Hydrocarbons.—The experimental evidence cited above lends support to the view that the following steps occur in the Fischer synthesis:



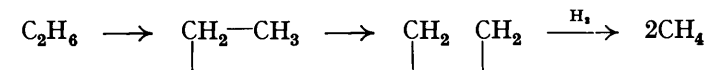
Separated CH₂ groups must be formed first because the carbon atoms in the carbide occur separated and not in ready-made chains (Jacobson and Westgren, *loc. cit.*), and it is quite unnecessary to introduce the complication that the hydrocarbon chains grow step by step by reaction of carbon monoxide and hydrogen at one end of them, because long-chain hydrocarbons can be produced from the carbides by dissolving them in acids, in which case such a mechanism is impossible. In the first place, therefore, a series of methylene groups are formed which can link up to form macro-molecules from which fragments can be broken off by suitable treatment. The presence of small quantities of branched-chain hydrocarbons can be readily accounted for on the assumption that occasionally a chemisorbed carbide can be incorporated in the macro-molecule, thus:



and if this is correct the branched-chain hydrocarbons produced should be tertiary rather than secondary.

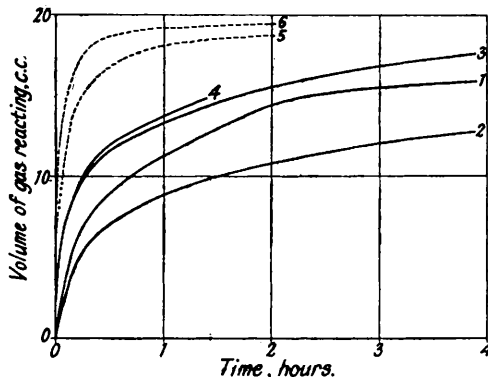
A clue to the mechanism of fragmentation of the macro-molecules formed by the above sequence of reactions is obtained by examination of the behaviour of the paraffin

hydrocarbons when brought into contact with a Fischer catalyst. Taylor and his co-workers (Morikawa, Benedict, and Taylor, *J. Amer. Chem. Soc.*, 1936, **58**, 1795; Morikawa, Trenner, and Taylor, *ibid.*, 1937, **59**, 1103) examined the reaction of ethane and propane with hydrogen on a nickel-kieselguhr catalyst and concluded that first of all chemisorption occurs with the carbon-carbon bonds left intact, then dissociative adsorption follows, with rupture of these bonds, and that only after this does reaction with hydrogen occur to give methane:



A similar reaction was found to occur when ethane, propane, or butane was mixed with the requisite amount of hydrogen and put in contact with the cobalt-thoria-kieselguhr Fischer catalyst at 200°, and curve (1) of Fig. 11 shows the rate of the reaction $\text{C}_3\text{H}_8 + 2\text{H}_2 \longrightarrow 3\text{CH}_4$. Both propane and butane yield small amounts of ethane, which is an intermediate stage in the reaction. When the hydrocarbons are put in contact with the catalyst without addition of hydrogen, a reaction also occurs to give methane and leaving carbon residues, either carbide carbon, $:\text{CH}$, $:\text{CH}_2$, or $\cdot\text{CH}_3$, on the catalyst, which can be

FIG. 11.
Rates of hydrogenation. Cracking of paraffin hydrocarbons.

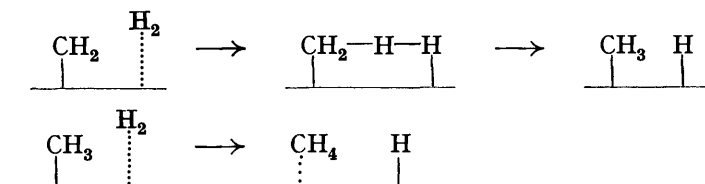


recovered as methane by further addition of hydrogen at 200°. Curves (2), (3), and (4) show the rates of this reaction for ethane, propane, and butane respectively, and curves (5) and (6) show the rates of reaction of the carbon residues with hydrogen after the reaction had been used for the reactions of curves (3) and (4). In this respect the Fischer catalyst resembles Taylor's nickel-kieselguhr catalyst rather than his cobalt-magnesium oxide catalyst (Taylor and Taylor, *ibid.*, 1939, **61**, 503) on which the hydrocarbons only react as $\text{C}_3\text{H}_8 + 2\text{H}_2 \longrightarrow 3\text{CH}_4$ and not as $\text{C}_3\text{H}_8 \longrightarrow 2\text{CH}_4 + \text{C}$.

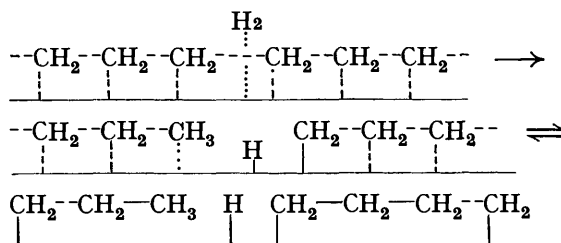
A Fischer catalyst has to be reduced by hydrogen at 375° before use, and if it is evacuated at this temperature for several hours it still contains sufficient hydrogen to yield some methane and chemisorbed carbon residues when it is put in contact with any of these hydrocarbons. If the last trace of hydrogen is removed by treating the catalyst with carbon monoxide or with ethane at 200°, however, these hydrocarbons can be added subsequently without any change, but on further addition of some hydrogen both methane and carbon residues are immediately formed. Hence, in contrast to the view of Taylor quoted above, it seems not unreasonable to assume that if hydrogenation-cracking is to occur on a Fischer catalyst at 200°, the presence of chemisorbed hydrogen is necessary. This conclusion is well supported by the results of the experiments on the ortho-para-hydrocarbons conversion, which showed that during the Fischer synthesis long-chain hydrocarbons are produced if the amount of chemisorbed hydrogen present is small, whereas methane is the product if the chemisorbed hydrogen is present in considerable quantities. It thus appears that the formation of methane, the chemisorption of ethane,

propane, or butane, and the breaking of paraffin or olefin chains on the catalyst surface, *i.e.*, the disrapture of fragments from the macro-molecules of CH_2 groups during the Fischer synthesis, all involve chemisorbed hydrogen. These reactions may be depicted as follows, where $-\text{X}$ represents a chemisorbed radical X, and $\cdots\text{Y}$ represents a molecule Y adsorbed by van der Waals forces.

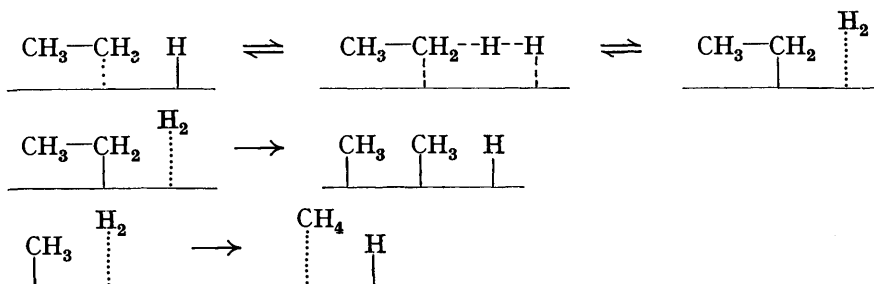
(i) The hydrogenation of a methylene group to methane :



(ii) Disrapture of a macro-molecule of CH_2 groups, only 6 such groups being shown in the macro-molecule, for convenience :



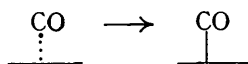
(iii) Chemisorption and hydrogenation-cracking of paraffin hydrocarbons :



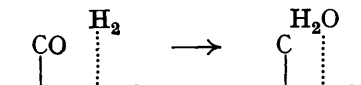
where $--$ stands for the partial valencies of a transition state.

Conclusions.—The evidence presented in this paper indicates that the mechanism of the Fischer synthesis involves the following steps.

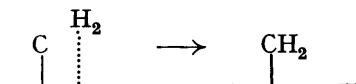
(i) Chemisorption of carbon monoxide :



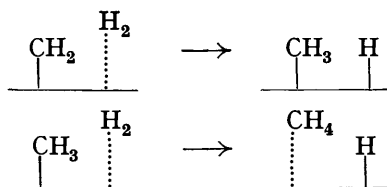
(ii) Reduction of chemisorbed carbon monoxide by hydrogen to give carbide :



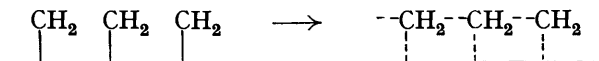
(iii) Reduction of the carbide to chemisorbed methylene groups :



If at this stage there is a large amount of chemisorbed hydrogen on the catalyst surface, the next step is (iva)



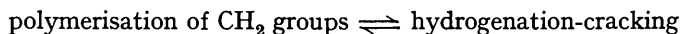
and methane is the product; but if, on the other hand, only a little chemisorbed hydrogen can be present, association of the methylene groups occurs to give macro-molecules:



(iv) These macro-molecules are then disrupted by interaction with hydrogen, probably as:

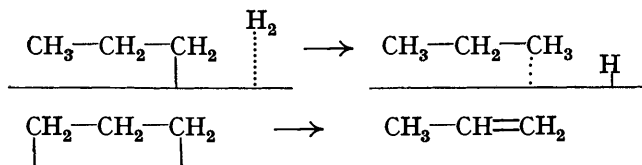


and the chain length of the products obtained will depend on the amount of hydrogen available for this process, which is given by the amount of chemisorbed hydrogen present on the surface. If much hydrogen is available, the equilibrium



is pushed over to the right-hand side and hydrocarbons of small chain length are formed, and conversely.

(v) Finally there is the desorption of the fragments of paraffins or olefins, probably as:



The normal initial period, when methane is being formed before the synthesis of oil sets in, is easily understandable on this basis, because the experimental evidence is that during the first few hours after admission of synthesis gas to the catalyst, carbide is being slowly built up. Since, during this time the catalyst will be incompletely covered with carbide and chemisorbed hydrogen can therefore be present on its surface, methane will be synthesised; but as less of the surface becomes available for chemisorbed hydrogen, so the formation of methane will diminish and the synthesis of oil set in. Ultimately, when the surface is completely covered with carbide to the complete exclusion of chemisorbed hydrogen, the synthesis will cease and the catalyst will be choked with heavy waxes as there is no means left for removing them from the surface. Hence revivification in hydrogen must be carried out before the synthesis can continue (see p. 1605). The more complicated initial behaviour described by Herington and Woodward (*loc. cit.*) is probably due to the fact that, when a freshly reduced catalyst is put in contact with synthesis gas at 180°, the activity of the most active spots on the catalyst is so high that their local temperature will rise considerably above that of the bulk of the catalyst, and hence methane will be formed just as it is formed when the bulk of the catalyst is maintained at 300°. If at this stage the temperature of the bulk of the catalyst is lowered to 150°, before the active spots became permanently sintered, and is then raised very slowly again in the way described by Herington and Woodward so that excessive temperature is not

developed on the active spots, synthesis of oil will set in, according to the normal mechanism already described. However, if the bulk temperature is allowed to remain at 190° for a long period of time, with the active spots much hotter and synthesising methane actively, these spots will sinter and hence will become relatively inactive towards carbon monoxide and will become permanently available for chemisorbed hydrogen, so that the product from such a catalyst will always be methane, even at 190°. This explanation agrees with an observation that when a naked thermojunction is put into the first layer of a freshly reduced catalyst and the synthesis gas is admitted at 190°, the temperature of this layer rises very markedly although the bulk temperature does not increase very much; and it also agrees with the fact that the abnormal initial behaviour has only been noticed with the most active modern catalysts, and that these only exhibit it when freshly reduced, but behave perfectly normally when put in contact with synthesis gas after revivification in hydrogen, because their previous period of use in synthesising oil will have reduced the activity of the very active spots to some degree, but without sintering them.

Subsequent experimental work on the functions of the promoters in the Fischer catalyst is in agreement with the present conclusions and will be published shortly.

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