

Cobalt-Nickel-Copper Catalysts

As the temperature of cobalt oxide was successfully reduced from 350° to 250° C. by the addition of more than 5 percent of copper, a similar application in the case of nickel catalysts was proposed. According to Fischer and Meyer^{73/} and Fujimura and Tsuneko,^{74/} copper is ineffective in lowering the reduction temperature of nickel; unless hydrogen reduction is carried out at 450° C., no liquid hydrocarbons are produced, and, even after such reduction, the yield is small. According to Fischer and Meyer,^{75/} when a Ni-Mn-Al₂O₃ catalyst containing only 0.1 percent copper (based on nickel) was reduced at 450° C., the yield of liquid hydrocarbons decreased rapidly from 120 to 84 ml./m.³ of synthesis gas. According to Fujimura and Tsuneko,^{76/} there is no increase in the yield of liquid hydrocarbons obtained from Ni-Mn catalyst containing up to 9.5 percent copper. At copper contents above 1 percent, the catalytic activity of nickel catalyst is impaired, whereas copper contents below 0.5 percent are ineffective in decreasing the reduction temperature of nickel. This difference in behaviour between cobalt and nickel catalysts was explained by Fischer^{77/} on the following basis. He postulated that copper has only an extremely weak tendency to form alloys with cobalt at synthesis temperatures; in cobalt catalysts, therefore, copper can function as a promoter. The ineffectiveness of copper as a promoter for nickel catalysts may be explained by one of the following mechanisms: (1) Either the reduction temperature of nickel oxide is lowered by the addition of copper, followed by combination of the reduced nickel with copper in any proportion to form mixed crystals, thereby destroying any catalytic properties suitable for this reaction, or (2) the reduction temperature of nickel is not lowered by the addition of copper, and, after reduction at high temperature, the nickel forms mixed crystals with copper with results comparable to (1).

From the observation that hydrogen reduction at 450° C. was necessary both when copper had been added and when copper had not been added to nickel catalysts, the author considered case (2) to be most probable. As the addition of cobalt to nickel catalysts did not impair their activities, an attempt was made to lower the reduction temperature of nickel catalysts by the addition of cobalt, the reduction temperature of which had been lowered by copper.

Results

The experimental results obtained by varying the proportion of cobalt to nickel and the proportion of copper with respect to the sum of cobalt and nickel in a Co-Ni-Cu-U₃O₈ catalyst are shown in table 27.

^{73/} Fischer, F., and Meyer, K., [The Reducibility of Standard Nickel Catalyst]: Brennstoff Chem., vol. 14, 1933, pp. 64-67.

^{74/} Work cited in footnote 48.

^{75/} Work cited in footnote 73.

^{76/} Work cited in footnote 48.

^{77/} Work cited in footnote 21.

TABLE 27. - Cobalt-nickel-copper catalysts

(Catalyst equivalent to 3 gm. of Co; gas velocity = 6 l./hr.)

Experiment No.	Catalyst composition				Reaction temperature, °C.	Volume gas used, l./hr.	Gas contraction, percent	Liquid products, ml./m. ³	
	Co	Ni	Cu	U ₃ O ₈				Gasoline (C ₅ +)	Water
62.....	50	50	0	12	190	72.0	84.5	145.6	205.2
63.....	80	20	10	12	200	72.0	80.2	140.5	200.0
64A.....	50	50	5	12	210	54.0	67.8	91.7	141.7
64B.....	50	50	5	12	220	54.0	70.2	116.6	175.0
65A.....	50	50	10	12	205	72.0	78.4	137.5	205.0
65B.....	50	50	10	12	215	72.0	76.8	120.8	198.2
66.....	20	80	10	12	215	36.0	53.2	66.6	106.6
67.....	20	80	20	12	220	36.0	55.6	60.0	98.8
68.....	10	90	10	12	220	36.0	-	-	-
69.....	10	90	20	12	220	36.0	-	-	-
70.....		80	20	12	220	36.0	-	-	-
71.....		50	50	12	220	36.0	-	-	-

Experiment 62. - Half the amount of cobalt in the catalyst used in experiment 49 was replaced by nickel. Following hydrogen reduction at 400° C. for 4 hours, synthesis gas was introduced at 190° C.; 145.6 ml. of gasoline (C₅+) and 205.2 ml. of water was produced per cubic meter of synthesis gas. These results do not differ greatly from those of experiment 49, and it is apparent that the catalytic nature of the cobalt was in no way impaired by the addition of nickel.

Experiment 63. - In this catalyst, 20 percent of the cobalt was replaced by nickel, and 10 percent copper (relative to Ni + Co) was added. After hydrogen reduction at 200° C. for 1 hour, synthesis gas was introduced, and 140.5 ml. of gasoline and 200.0 ml. of water were produced per cubic meter of synthesis gas. No significant difference between these results and those of experiment 52 (when nickel was not added) is evident. The reduction temperature of this cobalt catalyst was in no way affected by the substitution of 20 percent nickel.

Experiment 64A and B. - A catalyst containing a nickel:cobalt ratio of 1:1 and 5 percent copper was reduced in hydrogen for 1 hour at 200° C. Operation in the synthesis produced a gas contraction of 0 percent at 200° C., 12 percent at 210° C., and 60 percent at 220° C. After an hour at 220° C., the temperature was lowered to 210°, and the gas contraction remained at about 60 percent, clearly showing that a reduction temperature of 200° C. was inadequate. Hydrogen reduction was then carried out for 3 hours at 250° C., after which 91.7 ml. of gasoline and 141.7 ml. of water were produced at 210° C. per cubic meter of synthesis gas. Comparison with experiments 18A and B indicated that the activity of this catalyst was reduced considerably, suggesting that, at a copper content of 5 percent, the reduction of 1Ni:1Co catalyst was quite inadequate even after 3 hours at 250° C.

Experiment 65A and B. - The copper content of Ni:Co catalyst was increased from 5 percent to 10 percent. Synthesis gas was introduced after 1 hour's reduction at 200° C., producing a gas contraction of 60 percent at 200° and 80 percent at 210°, indicating that these conditions were nearly sufficient for complete reduction of this catalyst. After reduction for 1 hour at 250° C., 137.5 ml. of gasoline was produced per cubic meter of synthesis gas at a reaction temperature of 205° C., a value that decreased to 120.8 ml./m.³ at a reaction temperature of 215° C. These results are very similar to those of experiment 47, in which the catalyst contained no cobalt or copper and experiments 3 and 4, in which the catalyst contained no nickel. Thus, depending on the starting material, either half of the cobalt may be replaced by nickel in 100 Co:10 Cu:12 U₃O₈ catalyst, or half the nickel may be replaced by cobalt and 10 percent copper added to 100 Ni:12 U₃O₈ catalyst without any subsequent loss in catalyst activity, and, in the latter case, the necessary reduction temperature is decreased from 450° to 200° to 250° C.

Experiment 66. - Increasing the Ni:Co ratio to 8:2 in the presence of 10 percent copper and utilizing a reduction at 200° C. for 1 hour produced a gas contraction of 10 percent at 210° C. and 30 percent at 220° C. Reduction of the catalyst for 3 hours at 250° C. resulted in a gasoline yield of 66.6 ml. and a yield of water of 106.6 ml. per cubic meter of synthesis gas at a reaction temperature of 220° C. More complete reduction of the catalyst was thus indicated.

Experiment 67. - In this catalyst, the copper content was increased from 10 percent to 20 percent. However, after hydrogen reduction at 200° C., the resulting gas contraction was not large, and after hydrogen reduction for 3 hours at 250° C., only 60.0 ml. of gasoline and 98.8 ml. of water were produced per cubic meter of synthesis gas at 220° C.; therefore, a decrease in the activity of this catalyst from that exhibited by a catalyst containing 10 percent copper is evident. These results suggest that increasing the copper content from 10 percent to 20 percent decreases the reduction temperature of this catalyst still further, but that copper itself possesses no promoting characteristics as applied in this reaction. As in the general case of promoters, the addition of copper in excess of the optimum amount covers the active centers of the catalyst and gradually reduces its activity. A decrease in the reduction temperature of 8 Ni:2 Co catalyst by the addition of copper is accompanied by a loss in catalytic activity.

Experiments 68 and 69. - Increasing the Ni:Co ratio to 9:1 and the copper content to 20 percent produced no appreciable catalyst activity at reaction temperatures as high as 225° C. after reduction in hydrogen for 3 to 4 hours at 250° C.

Experiments 70 and 71. - These catalysts contained no cobalt, and copper contents of 10, 20, and 50 percent (based on the nickel) were tried. After reduction for 4 hours at 250° C., no activity could be detected at reaction temperatures as high as 230° C.

The above results show that the activity of Ni-Cu-U₃O₈ catalyst is not enhanced by the addition of cobalt, and that decreasing the reduction temperature of nickel oxide from 450° to 200° to 250° C. without simultaneously decreasing the activity requires the addition of an amount of cobalt equivalent to or greater than that of the nickel.

Recently, Tanaka and Kobayashi^{78/} concluded that the reduction temperature of nickel-copper catalysts is lower than that of either nickel or copper alone. According to Armstrong,^{79/} in the reduction of nickel-copper catalysts, copper oxide is first reduced; as this is an exothermic reaction, reduction of the nickel oxide is favored by the resulting heat of reaction. However, the activity of copper-containing catalysts depends largely upon the reduction conditions. For example, reduction of copper oxide in a rapid stream of hydrogen produces a white heat as a result of the exothermic nature of the reaction; the copper thus formed is very red, and its catalytic activity is extremely low. Conversely, reduction in a slow stream of hydrogen produces copper having a faint violet color and possessing a vigorous catalytic activity. On this basis, the reduction of Co-Cu-U₃O₈ and Ni-Cu-U₃O₈ catalysts may be considered to proceed first by the reduction of copper oxide; the reduction of the oxides of nickel and cobalt are then accelerated by the heat of reaction liberated at this time. The tendency to form mixed crystals of cobalt and copper is weak, but nickel and copper easily form mixed crystals, especially at local hot spots caused by the heat of reaction. Thus, the surface of the resulting catalyst is in a semi-sintered state, and its catalytic activity is extremely low. The reduction of cobalt oxide and nickel oxide in the absence of copper proceeds at 350° and 450° C., respectively. Therefore, a greater amount of energy must be released to accelerate the reduction of nickel oxide than is required to similarly affect cobalt oxide. Indeed, Co-Cu-Fe catalysts prepared by the calcination method become virtually inactive when reduced in hydrogen at 350° C.^{80/} Experimental results show that although the reduction of copper oxide accelerates the reduction of the nickel oxide component, insufficient energy is released by the copper oxide reaction to completely accomplish this objective. Is this conclusion compatible with the fact that the reduction temperature of nickel oxide was successfully lowered by the action of a large amount of cobalt and copper? Yes, because an additional source of heat is available from the conversion of cobalt oxide to cobalt. Copper oxide was first reduced, and its heat of reaction accelerated the reduction of cobalt oxide, with the result that more heat energy was released to accelerate the reduction of nickel oxide. A larger amount of cobalt oxide is needed to sustain its own reduction and that of nickel oxide as the proportion of copper oxide is decreased.

If, as the above discussion indicates, the reduction of nickel oxide-copper catalyst is incomplete at 250° C., the question is pertinent as to exactly what percent reduction is necessary for nickel, cobalt, and iron catalysts to make them good catalysts for the synthesis of liquid hydrocarbons from hydrogen and carbon monoxide. According to Anthoine,^{81/} iron catalysts

^{78/} Tanaka, Y., and Kobayashi, R., [High-Pressure Hydrogenation of Fatty Oils III. Production of Active Catalysts by Reduction of Mixed Hydroxides of Nickel and Copper in Liquid Medium]: Jour. Soc. Chem. Ind. Japan, vol. 36, 1933, p. 24; supplemental binding pp. 36-37.

^{79/} Armstrong, E. F., and Hilditch, T. P., Study of Catalytic Actions at Solid Surfaces IX. The Action of Copper in Promoting the Activity of Nickel Catalyst: Proc. Roy. Soc. (London), vol. 102A, 1922, pp. 27-32.

^{80/} Work cited in footnote 3.

^{81/} Anthoine, J., Decarriere, E., and Reaut, R., [Physicochemical Study of Iron Catalyst Used in the Synthesis of Liquid Hydrocarbons]: Chim. et Ind. Special No., vol. 31, 1934, pp. 421-423.

function in this catalytic capacity as Fe_3O_4 . However, nickel and cobalt catalysts react in a manner entirely different from that of iron catalysts; as their capacity for hydrogenation is high, they should be used in the form of mixtures of reduced metal and oxides. The hydrogenating ability of nickel catalysts is much superior to that of cobalt catalysts, and, when used for this purpose, nickel catalysts may be reduced, in the absence of diatomaceous earth, at about 300°C ., whereas, for cobalt catalysts a temperature of more than 400°C . is required. In the hydrocarbon synthesis, however, reduction of cobalt is carried out at 350°C ., whereas nickel requires a temperature of 450°C . Furthermore, whereas cobalt-copper catalysts can, without preliminary hydrogen reduction, initiate reaction with synthesis gas immediately, nickel-copper catalysts require previous hydrogen reduction at high temperatures. These observations suggest that the extent of reduction of nickel catalysts must be greater than that of cobalt catalysts for this reaction; in other words, the quantity of reduced metal relative to metal oxides in the nickel catalysts must be comparatively greater than in the case of cobalt catalysts.

Catalysts Containing Silver

It is well known that silver oxide can easily be used to separate metals by the application of heat at relatively low temperatures. This suggests that, like copper, silver can be added to cobalt oxide or to nickel oxide catalysts to lower their reduction temperatures. Accordingly, silver was added to cobalt oxide and nickel, and its effects upon them were observed. In preparing these catalysts, silver nitrate was used as a source of silver; nickel and cobalt carbonates were precipitated by potassium carbonate, and uranium oxide was used as a promoter.

Results

The results of these experiments are shown in tables 28 and 29.

Experiment 72. - This catalyst contained 10 percent of silver based on the cobalt. After hydrogen reduction for an hour at 200°C ., synthesis gas was introduced; gas contractions of 0 percent at 200° , 20 percent at 210° , and 60 percent at 230°C . were found. These poor results were attributed to inadequate reduction, so the catalyst was reduced for 2 hours at 250°C . As a result, at 180°C . 154.2 ml. of gasoline (C_{5+}) was produced per cubic meter of synthesis gas. Comparison of these results with those of experiments 3 and 4, in which 10 percent of copper was added, shows that silver is inferior to copper in lowering the reduction temperature of cobalt oxide, as the copper-containing catalyst was reduced successfully at 200°C ; on the other hand, whereas the reaction temperature of the copper-containing catalyst was 210°C ., the silver-containing catalyst exhibited an adequate activity at the relatively low temperature of 180°C ., whereas the yield of gasoline was increased considerably. Thus, silver is superior to copper as promoter.

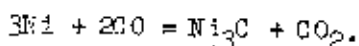
Experiment 73. - In this catalyst, the silver content was increased to 20 percent, resulting in a satisfactory activity after hydrogen reduction for an hour at 200°C . At a reaction temperature of 180°C ., 148.2 ml. of gasoline was produced per cubic meter of synthesis gas, a result not materially different from that obtained with the catalyst containing 10 percent silver.

Experiment 74. - This catalyst contained 10 percent silver based on the nickel. Hydrogen reduction was carried out for 3 hours at 250° C., and a gas contraction of 38 percent was obtained at a reaction temperature of 210° C. After more strenuous reduction for 1 hour at 300° C., this catalyst yielded a gas contraction of only 58 percent with a gasoline yield of only 28.6 ml./m.³ of synthesis gas, and it is evident from the composition of the product gases that the greater part of the carbon monoxide was converted to carbon dioxide and gaseous saturated hydrocarbons. From previous observations, a decrease in the reaction temperature may be expected to increase the amount of gasoline produced. When the temperature was lowered to 200° and 190° C., the gas contraction decreased rapidly to 42 and 26 percent, respectively; and when 36.0 liters of synthesis gas was used, the respective gasoline yields were 38.2 ml. at 200° and 20.5 ml. at 190° C. per cubic meter of synthesis gas. Considering that similar catalysts containing 10 percent copper showed no activity at reaction temperatures up to 230° C., silver is superior to copper as an agent for lowering the reduction temperature of nickel oxide.

Experiment 75. - The silver content of the catalyst was increased to 20 percent, and hydrogen reduction was carried out for 1 hour at 300° C. The results are poorer than those for catalysts containing 10 percent silver; the gas contraction was only 34 percent at 220° C., and only a trace of gasoline was produced.

MECHANISM OF THE HYDROCARBON SYNTHESIS

Although no definite experimental evidence exists to support any postulated reaction mechanism for the synthesis of olefin and paraffin hydrocarbons from carbon monoxide and hydrogen, Fischer's carbide theory is considered the most probable. According to this theory, carbon monoxide first combines with either the nickel or the cobalt in the catalyst to form nickel or cobalt carbide. This carbide reacts with hydrogen to form free radicals, such as CH-, CH₂, and CH₃, which polymerize and take on hydrogen to form various olefin and paraffin hydrocarbons. The formation of carbide and carbon dioxide from nickel, cobalt, or their oxides and carbon monoxide has been established. Thus, the reaction between nickel and carbon monoxide is represented by:



Although Fischer's mechanism postulates that free radicals polymerize and that the production of liquid hydrocarbons is accompanied by a large production of carbon dioxide without the formation of water, direct experimental results show that approximately 1-1/2 times more water than oil is produced, and no more than 2 or 3 percent of carbon dioxide is obtained under normal circumstances.

To explain this, Fischer stated that in the synthesis of liquid hydrocarbons the union of carbon and oxygen in carbon monoxide was first severed in the presence of nickel or cobalt catalyst, at which time the carbon combined with the activated metal to form carbides, and the oxygen reacted immediately with activated hydrogen to form water. However, various investigators, who passed carbon monoxide over nickel or cobalt with the formation of carbide, then passed hydrogen over the carbide and obtained the carbon of the carbide principally as gaseous hydrocarbons (chiefly methane); no liquid hydrocarbons were observed.

Any explanation for catalytic activity is generally based on the presumption that the reaction takes place via an intermediate compound formed between the catalyst and the reactants. However, considering that the amount of active catalyst existing at any one time is extremely small (for instance, in the reaction, $C_6H_5NO_2 + 6H_2 = C_6H_{11}NH_2 + 2H_2O$, when reduced nickel is used, the probable amount of active nickel engaged in the reduction is 0.385 percent;^{82/} whereas, when ammoniated iron-alumina catalyst is used, the amount of active iron element is 0.25 percent;^{83/}), it is evident that the formation of carbides at these active centers and their reaction with hydrogen would result in the formation of quantities of liquid hydrocarbons so small that they could hardly be detected. Furthermore, comparison of the case where carbon monoxide and hydrogen co-exist with the case where carbon monoxide does not exist, but where only hydrogen and carbide co-exist, shows a great difference between the equilibrium relationships in the two cases. The validity of either theory cannot immediately be judged, therefore, on the basis of the experimental results previously described.

Formation of Carbides

Much research has been carried out on the reaction of carbon monoxide with nickel, cobalt, iron, and their oxides. Bahr and Bahr^{84/} maintained that at temperatures below 270° C. nickel and carbon monoxide react quantitatively to form Ni_3C and that at increased temperatures Ni_3C (in this case metallic nickel does not exist at all) reacts still further with carbon monoxide to form Ni_xC and carbon dioxide. At temperatures above 380° to 420° C., Ni_3C decomposes into nickel and carbon, and this nickel is postulated as accelerating the decomposition of carbon monoxide.

In this respect, Horiba and Ri^{85/} made the following claims:

1. Ni_3C is formed only at the active centers of the catalyst.
2. Because of the formation of Ni_3C , catalysis of the decomposition of carbon monoxide is reduced.
3. Carbon monoxide reactions take place only on the remaining active centers of the nickel surface.

According to Tutsiya,^{86/} at temperatures below 285° C., nickel and nickel oxide react with carbon monoxide to form Ni_3C and Ni_xC . Nickel on the surface

^{82/} Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 31, 1925, p. 223.
(Reference could not be located.)

^{83/} Alquist, J. A., The Nature of the Catalyst Surface and the Effect of Promoters: Jour. Am. Chem. Soc., vol. 48, 1926, pp. 2820-2826.

^{84/} Bahr, E. A., and Bahr, Th., [Decomposition of Carbon Monoxide on Nickel]: Ber., vol. 61B, 1928, pp. 2177-2183; [Reactions of Nickel Carbide (Ni_3C) Prepared at Low Temperatures]: Ber., vol. 63B, 1930, pp. 99-102.

^{85/} Horiba, S., and Ri, T., [Taylor's Theory of Active Centers and the Kinetics of Heterogeneous Gaseous Reactions]: Rec. trav. chim., vol. 51, 1932, pp. 641-647.

^{86/} Tutsiya, R., [Catalytic Decomposition of Carbon Monoxide IV. Behaviour of Nickel Carbides]: Bull. Inst. Phys. Chem. Research (Tokyo), vol. 10, 1931, pp. 951-973.

of the Ni_3C adsorbs the carbon monoxide; at temperatures of 265° to 275° C. carbon monoxide is adsorbed only in the presence of Ni_3C . Tutiya stated that in this case the process $Ni \xrightarrow{CO} Ni_3C \xrightarrow{CO} Ni_xC \rightarrow Ni_3C + C$ existed. Ni_xC (nickel supercarbides) are extremely unstable, decomposing rapidly at about 280° C., and the pyrophoric nature of nickel carbide is really a result of this reaction.

Fischer, in his experiment, ^{87/} reacted cobalt with carbon monoxide to form Co_3C_2 and obtained hydrocarbons from the carbide corresponding only to Co_3C . Tutiya ^{88/} found Fe_3O_4 and Fe_3C (also carbides of other indefinite forms) when reacting iron oxide and carbon monoxide at 320° C. but did not find Fe_3O_4 or Fe_xC (supercarbides) at 270° C. In other words, Tutiya postulated that at temperatures above 280° C. such processes as $Fe_2O_3 \xrightarrow{CO} Fe_3C \xrightarrow{CO} Fe_xC \rightarrow Fe_3C + C$ exist.

From the above experimental evidence, there is no doubt that carbon monoxide reacts with nickel, cobalt, or iron to form carbides of special composition. The speed of formation of such carbides is greatly influenced by the condition of the metal surface and by the method of its preparation. That is, the greater the activity of the catalyst, the lower the temperature and the greater the rate at which carbide is formed. The observation has previously been made that when mixtures of carbon monoxide and hydrogen are used a marked change in reaction mechanism occurs, and the characteristic production of carbon dioxide is replaced by a production of water. It must be emphasized that this is true only in the case of cobalt and nickel catalysts. When iron catalysts are used, carbon dioxide is the characteristic product, whether pure carbon monoxide or a carbon monoxide-hydrogen mixture is used. Thus, in the case of nickel or cobalt catalysts:



and in the case of iron catalysts:



In order that both reactions (1) and (2) may proceed from left to right, the bonds in the carbon monoxide molecule and the hydrogen molecule must be broken. In addition, the attraction between carbon and hydrogen atoms, between hydrogen and oxygen atoms, and between a molecule of monoxide and an oxygen atom must be greater than the energies of the bonds that are broken. The forces that promote formation of water and those that promote formation of carbon dioxide differ according to the catalyst used. To promote formation of water, a catalyst that activates hydrogen atoms must be chosen; conversely, a catalyst that activates the carbon monoxide molecule must be used if carbon dioxide is to be produced.

^{87/} Fischer, F., [Collected Papers on the Knowledge of Coal]: Vol. VIII, G. Borntraeger, Berlin, 1927, p. 255.

^{88/} Tutiya, H., [Catalytic Decomposition of Carbon Monoxide III. Behaviour of Iron Carbides]: Bull. Inst. Phys. Chem. Research (Tokyo), vol. 10, 1932, pp. 556-562; abstracts (in English) published in Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 16, Nos. 306-309, 1931.

Anthsaune⁸⁹/ stated that because iron catalysts are used successfully in the form of Fe_3O_4 , whereas nickel and cobalt catalysts must first be reduced at $350^\circ C.$ to $450^\circ C.$, the difference in the nature of reactions (1) and (2) lies in the presence or absence of reduced metals in the catalysts.

Formation of Free Radicals

When nickel, cobalt, or iron catalysts are carburized with carbon monoxide, and when hydrogen is passed over these carbides, gaseous hydrocarbons, the main constituent of which is methane, are formed, with the complete exclusion of liquid hydrocarbons. The composition of these products, consisting of straight-chain paraffin or olefin hydrocarbons almost entirely, suggests that their formation proceeds via such free radicals as $\dot{C}H$, $\dot{C}H_2$, and $\dot{C}H_3$, and that these building units are produced by some reaction between carbon monoxide and hydrogen.

As the hydrogenation of carbide produces methane, it is not difficult to conjecture that, while hydrogen is being added to form methane, the steps, $C \rightarrow \dot{C}H_2 \rightarrow \dot{C}H_3 \rightarrow \dot{C}H_4$ exist. The amount of these free radicals formed depends to a great extent on the reaction temperature and the composition of the catalyst. To form high-molecular-weight liquid hydrocarbons by such a process, much polymerization must occur before hydrogen is added to stop the reaction. The addition of hydrogen to a particle of only a few building units ($\dot{C}H_2$) effectively stops the polymerizing action on that particle, and, if this is a general case, only gaseous hydrocarbons are produced. In other words, a catalyst for the synthesis of gasoline and long-chain hydrocarbons must be more active as a polymerization catalyst than as a hydrogenation catalyst.

Because nickel and cobalt catalysts have high hydrogenating capacities, the formation of gaseous hydrocarbons is always great at the beginning of the synthesis; the production of liquid hydrocarbons is small and becomes significant only after 2 or 3 hours. The author infers that this loss of hydrogenating capacity is accompanied by an increase in polymerizing capacity of nickel or cobalt catalysts, and that it occurs as nickel carbide or cobalt carbide is formed at the active centers of the catalyst. (That is, in the boundary surface between the carbide and the reduced metal, carbide is considered as some sort of polymerization accelerant.) On this basis, a simple explanation may be advanced for the large production of gaseous hydrocarbons that occur during the first stages of synthesis and for the increased production of gaseous hydrocarbons with increase in temperature. For example, if nickel or cobalt catalysts, which have never been processed in reactions, are treated with carbon monoxide-hydrogen mixtures at about $200^\circ C.$, most of the carbides produced in these catalysts by reaction with carbon monoxide are decomposed largely into methane and metallic nickel or cobalt by reaction with hydrogen; those carbides that are relatively difficult to react with hydrogen at about $200^\circ C.$ remain. The amount of residual carbides of this type increases with reaction time until, after a given time, the quantity of carbide decomposed by hydrogen equals the quantity of carbide regenerated by the carbon monoxide. The reaction has then attained a constant state, and definite amounts of carbide and reduced nickel or cobalt exist in the catalyst at all times. Because of the inhibiting effect of the carbides on the hydrogenating ability of these metals, a large production of liquid hydrocarbons is obtained.

⁸⁹/ Work cited in footnote 81.

The carbide:reduced-metal ratio finally achieved is dependent upon the CO:H₂ ratio in the synthesis gas and the reaction temperature. A surplus of hydrogen reduces the quantity of residual carbide and accelerates the formation of gaseous hydrocarbons; a similar effect is achieved with increase in reaction temperature, which increases the reactivity of hydrogen and carbide.

From these observations, it would be concluded that the greater the surplus of carbon monoxide and the lower the reaction temperature, the more the synthesis of liquid hydrocarbons would be favored. Actually, however, exceeding a certain residual-carbide:reduced-metal ratio decreases the regeneration of carbides on the reduced metal, and, hence, a maximum in the production of liquid hydrocarbons cannot be avoided.

As carbides of this type are easily decomposed by hydrogen, the hydrogenation capacity can be increased by increasing the reaction temperature to a suitable degree. However, although the formation of carbides is decreased, because such reactions as $Ni_3C \xrightarrow{CO} Ni_xC \rightarrow xNi + C$ occur at elevated temperatures, free carbon, which is relatively difficult to react with hydrogen, is generated and deposited on the active surface of the catalyst. Thus, the hydrogenation reaction, the rate of which is great in the early stages of synthesis, loses its activity rapidly.

The temperature at which free carbon is produced depends, of course, on the type of catalyst employed and on the composition of the synthesis gas. The quantity of free carbon deposited in the catalyst increases with time and plays an important role in the deterioration of catalyst activity.

Production of Liquid Hydrocarbons from Carbon Dioxide and Hydrogen

The synthesis of liquid hydrocarbons by the catalytic reduction of carbon dioxide was studied by Fischer and Pichler^{90/} and Koch and Küster^{91/} and many others, but in all cases methane was produced instead of gasoline. According to Fischer,^{92/} when nickel-alumina catalyst is used in the methane synthesis, the reduction of carbon dioxide begins at 200° C. whereas the reduction of carbon monoxide does not occur until about 250° C. is reached. However, in the synthesis of liquid hydrocarbons, the carbon dioxide in synthesis gas mixtures of carbon monoxide, hydrogen, and carbon dioxide has no effect whatever on the yield and, without further addition of hydrogen, appears as such in the product gas; the hydrogenation of carbon dioxide is initiated only after any carbon monoxide is totally consumed.

The author has inferred that liquid hydrocarbons are formed under conditions where the hydrogenation capacity of a catalyst is somewhat restricted by carbides produced in the catalyst by reaction with carbon monoxide. Parallel

^{90/} Fischer, F., and Pichler, H., [The Simultaneous Effect of Carbon Monoxide and Carbon Dioxide During Hydrogenation, with Particular Regard to the Synthesis of Hydrocarbons]: Brennstoff Chem., vol. 14, 1933, pp. 306-310.

^{91/} Koch, H., and Küster, H., [The Catalytic Reduction of Carbon Dioxide with Hydrogen]: Brennstoff Chem., vol. 14, 1933, pp. 245-251.

^{92/} Work cited in footnote 90.

reasoning suggests that as carbon dioxide does not enter into any chemical reaction with reduced nickel or cobalt (of course, reduced nickel and cobalt absorb and desorb carbon dioxide at rates which are in equilibrium), no inhibitive effects on its hydrogenation should be considered by virtue of the presence of carbides. Therefore, the carbon dioxide should readily be hydrogenated to methane. However, it has been shown experimentally that at temperatures necessary for appreciable reduction of carbon dioxide all carbon monoxide is quickly consumed by the hydrocarbon synthesis mechanism.

SUMMARY

1. Studies were made of the effects of reaction temperature, gas velocity, and synthesis gas composition on the yield of liquid hydrocarbons, and an optimum reaction temperature and gas velocity were found to exist. A compromise between the most desirable yield of liquid hydrocarbons and the greatest catalyst durability was established at a $H_2:CO$ ratio of 2:1.
2. A ratio of diatomaceous earth to the metals content of the catalyst was found to produce the best results between 1:1 and 3:4; silica gel was also found to be a fair carrier.
3. In the preparation of catalysts, acetates were found to be as good a source material as nitrates.
4. Studies of nickel catalysts showed that by using 100 Ni:20 Mn:8 U_3O_8 :4 ThO_2 catalyst, 168.8 ml. of gasoline (C_{5+}) was obtained per cubic meter of synthesis gas.
5. Cobalt-copper catalysts and nickel-cobalt-copper catalysts were investigated. The temperature at which cobalt is reduced does not impair its subsequent catalytic activity in any way. The reduction temperature of cobalt may be lowered from 350° to 200° C. by the addition of more than 5 percent copper; to lower the reduction temperature of nickel from 450° to 250° C., more than 100 percent cobalt and more than 10 percent copper (relative to the nickel) must be added.
6. Studies of catalysts containing silver showed that although silver is inferior to copper as a means of lowering the reduction temperature, it is superior to copper as a promoter.
7. The mechanism of the hydrocarbon synthesis was discussed.

A REVIEW OF INTERNATIONAL RESEARCH ON THE HYDROCARBON SYNTHESIS

Germany

The discovery of the synthesis of hydrocarbons from carbon monoxide and hydrogen is generally credited to Fischer and his associates at Muhlheim, Germany. In 1923, Fischer and Tropsch^{23/24} reduced carbon monoxide

^{23/} Fischer, F., and Tropsch, H., [The Preparation of Synthetic Oil Mixtures (Synthol) from Carbon Monoxide and Hydrogen]: Brennstoff Chem., vol. 4, pp. 276-285.

^{24/} Fischer, F., and Tropsch, H., [Preparation of Synthetic Oil (Synthol) from Carbon Monoxide and Hydrogen]: Brennstoff Chem., vol. 5, 1924, pp. 201-206, 217-227.

catalytically at high pressures. Using scrap iron containing alkali, particularly rubidium carbonate, as a catalyst at 400° to 450° C. and 75 to 100 atmospheres' pressure, these workers obtained reaction products containing 10 percent acidic substances, 29 percent of water-soluble alcohols, aldehydes, and ketones, 11 percent of water-soluble oils, and 48 percent of water-insoluble materials. This product they called "synthol." By treatment at 450° C. and high pressures, "synthine," composed chiefly of hydrocarbons, was obtained and proved usable as a substitute for gasoline. Reduction of carbon monoxide was then studied at normal pressures.

Laboratory Research

In 1926, Fischer and Tropach^{95/} tested oxides of chromium, zinc, beryllium, rare earth elements, uranium, and magnesium as promoters for iron and cobalt catalysts. They found that the activity was greatest at metal:oxide ratios of 1:1 or 3:1. At about 270° C., 1 cubic meter of water gas ($H_2:CO = 1:1$) was repeatedly passed over the catalyst to yield approximately 100 gm. of oil (liquid hydrocarbons).^{96/} Because water gas deactivated the catalyst quite rapidly, coke-oven gas was reacted with steam at high temperatures to give synthesis gas ($H_2:CO = 2:1$). The most suitable catalyst was found to be 100 Fe:25 Cu:2 K_2CO_3 or 9 Co:1 Cu; 20 to 25 ml. of gasoline (C_{5+}) was obtained with a single pass per cubic meter of synthesis gas. In 1930, Berl and Jüdling^{97/} studied iron and cobalt catalysts containing copper, zinc oxide, manganese oxide, and potassium carbonate. They found that under their conditions the activity of cobalt catalysts was greater than that of iron catalysts. The same year Fischer^{98/} found that the presence of alkali was favorable in iron-copper catalysts. By adding a small amount of manganese oxide and alkali to a catalyst of composition Fe:Cu = 4:1, he obtained 40 to 45 ml. of gasoline per cubic meter of $2H_2:1CO$ gas; a gasoline yield of 100 ml./m.³ was obtained with 9 Co:1 Cu:2 Th catalyst.

It was then discovered that by mixing 2 $H_2:1CO$ gas and 1 $H_2:1CO$ gas, and using it in the synthesis at a low velocity, a gasoline yield of 50 ml./m.³ mixed gas was obtained with iron catalyst and a yield of 130 ml./m.³ was obtained with cobalt catalyst. Highly porous substances, such as Stüttgartermasse, were used as carriers for the catalysts in these cases.

In 1931, Fischer and Meyer^{99/} investigated nickel catalysts and found that thorium and manganese were superior promoters for nickel. Catalysts precipitated from mixed solutions of nitrate salts by sodium bicarbonate or potassium carbonate were most superior, exhibiting an activity comparable to that obtained with catalysts prepared by the calcination of nitrate salts. These investigators advocated using diatomaceous earth as a carrier. In nickel-thorium catalysts, a composition of 100 Ni:18 $ThO_2:100$ diatomaceous earth, obtained by precipitating from a solution of mixed nitrate salts by potassium carbonate, had the greatest activity, the gasoline (C_{5+}) yield was 120 ml./m.³ of synthesis gas. Tests of sodium carbonate, potassium carbonate, ammonium carbonate, caustic potash, and caustic soda showed potassium carbonate to be the best precipitant, with sodium bicarbonate second best;

^{95/} Work cited in footnote 6.

^{96/} Work cited in footnote 21.

^{97/} Work cited in footnote 11.

^{98/} Work cited in footnote 21.

^{99/} Work cited in footnote 12.

caustic potash and caustic soda produced catalysts with almost no activity. Hydrogen reduction was found to be most suitable at 450° C. for 3 hours. Studies of the durability of nickel-thoria catalysts showed that after 5 weeks' use the yield of gasoline was reduced by 12 percent.

In the preparation of nickel-manganese catalysts, potassium carbonate was found to be the best precipitant. A gasoline yield of 120 ml./m.³ of synthesis gas was obtained by using a composition of 100 Ni:20 Mn:100 diatomaceous earth; addition of a small quantity of alumina increased this to 130 ml./m.³.

In 1932, Fischer and Koch¹ studied cobalt catalysts. Corresponding to the results obtained with nickel, thoria and manganese were found to be superior promoters, and, in cobalt-thoria catalysts, potassium carbonate was the best precipitant. A gasoline yield of 153 ml./m.³ of synthesis gas was obtained by using a composition of 100 Co:18 ThO₂:150 diatomaceous earth. Hydrogen reduction was found to be most suitable at 350° C. for 4 to 5 hours. In cobalt-manganese catalysts, sodium bicarbonate was found to be superior to potassium carbonate as a precipitant; a gasoline yield of 144.5 ml./m.³ of synthesis gas was obtained using a 100 Co:15 Mn:150 diatomaceous earth catalyst.

In 1933, Fischer and Meyer² used 100 Ni:20 Mn:10 Al₂O₃:100 diatomaceous earth catalyst as a standard catalyst in the synthesis of liquid hydrocarbons and clarified the optimum conditions for the precipitation and water wash in the preparation of the catalyst. To a mixed-nitrate solution corresponding to 5 gm. of nickel, potassium carbonate was added, and the resulting precipitate was washed four or five times with 100 ml. of hot water (it was found desirable to leave a minute amount of alkali in the catalyst). Neither graphite (which is considered a good conductor of heat) nor silica gel substances other than diatomaceous earth were found suitable for catalyst carrier purposes. Potassium carbonate was found to be an excellent precipitant. Potato starch was mixed into the catalyst with water, and this material was granulated, placed in the reaction tube, and reduced in hydrogen containing ammonia; a gasoline yield of 140 ml./m.³ of synthesis gas was obtained.

Koch and Kuster³ utilized nickel and cobalt catalysts for the synthesis of gasoline. Attempted reduction of carbon dioxide at various reaction temperatures, and gas compositions yielded no liquid hydrocarbons. Fischer and Pichler⁴ observed the effect of carbon dioxide in the synthesis gas; 5 to 10 percent of carbon dioxide was found to have no effect on the yield of liquid hydrocarbons.

In 1934, Fischer and Meyer⁵ made a study of alloy catalysts and found that the catalyst obtained by dissolving out aluminum and silicon by means of caustic soda from alloys consisting of nickel or cobalt (or their mixtures) and aluminum or silicon could be utilized in this reaction. Using 4 gm. of Co-Ni catalyst, 90 ml. of gasoline per cubic meter of synthesis gas was obtained. When this method of preparation was applied to iron catalysts, the

¹/ Work cited in footnote 3.

²/ Work cited in footnote 37.

³/ Work cited in footnote 91.

⁴/ Work cited in footnote 90.

⁵/ Fischer, F., and Meyer, K., [Alloy Skeletons as Catalysts for the Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen]: Brennstoff Chem., vol. 15, 1934, p. 107; Ber., vol. 67B, 1934, pp. 253-261.

results were poor. This type of alloy catalyst has the disadvantage of being less active than precipitated catalysts and of lacking durability; however, it also has the advantage that the activity can be regenerated easily in the event that the catalyst is contaminated with sulfur.

Fischer and Koch^{6/} and Wiedeking^{7/} studied the production of lubricating oils from the olefins contained in synthesis gasoline.

Pilot-Plant Work

In 1930, Fischer^{8/} conducted an experiment on a pilot-plant scale using a synthesis gas obtained by mixing 2 H₂:1 CO gas and 1 H₂:1 CO gas. The gas was purified by removing hydrogen sulfide with iron oxide; organic sulfur compounds were converted into hydrogen sulfide by passage through iron pipes heated to 400° C., and this was scrubbed out in a solution of prussiate salts. The synthesis reaction is violently exothermic, and, as increase in temperature promotes the formation of such gaseous hydrocarbons as methane, ethane, and propane, the heat of reaction had to be dissipated rapidly to prevent the temperature of the catalyst from rising. Fischer paid special attention to this point and tried various reactor chambers.

In 1932, Fischer, Roelen, and Feisst^{9/} utilizing 100 Ni:20 Mn:10 Al₂O₃:100 diatomaceous earth catalyst and a synthesis gas similar to that just described, conducted an experiment on a pilot-plant scale. A revolving gas-heated reaction tube 155 mm. in diameter and 450 mm. long was used; 890 gm. of catalyst was employed at a reaction temperature of 190° to 200° C., and a gas velocity of 100 liters per hour was used. The results showed a gas contraction of 60 percent and a gasoline (C₅₊) yield of 80 ml. (65 gm.) per cubic meter of synthesis gas; this value was less than the yield (120 ml./m.³) obtained in the laboratory and was probably due to the highly variable temperature distribution within the reaction tube. Better results were obtained by decreasing the diameter and increasing the length of the reaction tube and by heating it in an electrically heated oil bath instead of with a gas flame. With 70 liters (21.3 kg.) of catalyst at reaction temperatures of 190° to 200° C. and a gas velocity 6.8 m.³/hr., 100 ml. (70 gm.) of gasoline was obtained per cubic meter of synthesis gas, results as good as those obtained in the laboratory (100 ml./m.³) under these conditions. After 1,000 hours' operation, a large amount of solid paraffins collected on the catalyst, necessitating its reactivation by extraction of solid paraffins with gasoline or benzene followed by reduction in hydrogen at 450° C.

6/ Fischer, F., and Koch, H., [The Synthesis of Lubricating Oils from Kogasin. Preliminary Communication]: Brennstoff Chem., vol. 14, 1933, pp. 463-466.

7/ Fischer, F., Koch, H., and Wiedeking, K., [Advances in the Preparation of Lubricating Oils, Starting with Kogasin]: Brennstoff Chem., vol. 15, 1934, pp. 229-233.

8/ Work cited in footnote 21.

9/ Fischer, F., Roelen, C., and Feisst, W., [The Present Technical Position of the Hydrocarbon Synthesis]: Brennstoff Chem., vol. 13, 1932, pp. 461-468.

The extensive nature of the studies conducted in Japan on the hydrocarbon synthesis is second only to those made in Germany. The work had its start with Kodama's^{10/} study at the Kita Laboratory of Kyoto Imperial University. In 1929, the catalytic characteristics of iron, copper, cobalt, and nickel were determined with regard to mixtures of equal volumes of carbon monoxide and hydrogen. These results demonstrated that copper had no catalytic activity, that addition of alumina and manganese oxide to cobalt was deleterious to its activity, that the addition of thorium and copper retarded the decomposition of carbon monoxide ($2CO = C + CO_2$), and that the addition of potassium carbonate accelerated the decomposition of carbon monoxide. The same year, Kobayashi and Yamamoto^{11/} utilized $100Co_2O_3:50CuO:75MnO$ catalyst and Kodama^{12/} utilized $3 Co:1 Cu:0.45ThO_2$ catalyst and obtained, respectively, gasoline yields of 4.9 ml. and 10.2 ml. per cubic meter of 1 $H_2:1CO$ gas. In 1930, Kodama,^{13/14/} using cobalt and copper catalysts containing $BeO, MgO, ZnO, CaO, TiO_2, ZrO_2,$ and CoO_2 , found that MgO was the best promoter and that the addition of alkali carbonates to iron-copper catalysts was beneficial.^{15/16/} With $3 Co:1 Cu:0.45 Mn$ and $100 Fe:10 Cu:2 Na_2CO_3$ catalysts, gasoline yields of 14.8 ml. and 21.2 ml., respectively, were obtained per cubic meter of 1 $H_2:1 CO$ gas.

In 1931, Kodama and Fujimura^{17/} settled on an iron-copper catalyst of composition $100 Fe:100 Cu:0.5 Na_2CO_3$ as the best. The same year Fujimura^{18/} found that variation of the iron:copper ratio from 5:1 to 2:1 produced almost no change in the yield of gasoline. A cobalt-copper-magnesia catalyst of composition $Co:Cu:MgO = 4:1:1$ was determined as the most suitable of this type, yielding 46.6 ml. of gasoline per cubic meter of 1 $H_2:1 CO$ gas.^{19/}

^{10/} Work cited in footnote 70.

^{11/} Kobayashi, K., and Yamamoto, K., [Synthesis of Petroleum Hydrocarbons from Hydrogen and Carbon Monoxide at Ordinary Pressure]: Jour. Soc. Chem. Ind. Japan, vol. 32, 1929, p. 54.

^{12/} Work cited in footnote 9.

^{13/} Kodama, S., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure IV. Influence of Beryllium Oxide, Magnesium Oxide, Zinc Oxide, and Cadmium on Cobalt-Copper Catalysts]: Jour. Soc. Chem. Ind. Japan, vol. 33, 1930, p. 161; supplemental binding p. 60.

^{14/} Work cited in footnote 51.

^{15/} Work cited in footnote 13.

^{16/} Kodama, S., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure VI. The Formation of Hydrocarbons by Iron Catalysts]: Jour. Soc. Chem. Ind. Japan, vol. 33, 1930, p. 1150; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 14, No. 269, 1930, pp. 169-183 (in German).

^{17/} Kodama, S., and Fujimura, K., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure VII. Effect of Alkalies on Iron-Copper Catalysts]: Jour. Soc. Chem. Ind. Japan, vol. 34, 1931, p. 32; supplemental binding pp. 14-16 (in German).

^{18/} Fujimura, K., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure VIII. The Iron-Copper Catalyst]: Jour. Soc. Chem. Ind. Japan, vol. 34, 1931, p. 366; supplemental binding pp. 136-138.

^{19/} Work cited in footnote 33.

In 1932, Fujimura,^{20/} investigating the effect of thorium, uranium, molybdenum, tungsten, chromium, and cerium on cobalt-copper-magnesium catalysts, found thorium and uranium to be the best promoters and obtained a gasoline yield of 81.5 ml. per cubic meter of 2 H₂:1 CO gas in the presence of 8 Co:1 Cu:2 Mg:9.4 U catalyst. In the preparation of Co-Cu-Th and Co-Cu-U catalysts, addition of starch to mixed nitrate salts, followed by evaporating, drying, and calcining, yielded a catalyst of large bulk volume. The largest gasoline yield was obtained with 8 Co:1 Cu:0.5 Th:0.15 U catalyst, the yield of gasoline in this case being 141.0 ml. per cubic meter of synthesis gas; by varying the proportions of thorium and uranium, this value was increased to 145 ml./m.³. In 1933, Fujimura and Tsuneoka^{21/} observed that the addition of a minute amount of potassium carbonate (about 0.05 percent) to the nickel in nickel-thoria catalysts promoted their activities; conversely, potassium carbonate was found to be harmful to the activities of nickel-manganese catalysts. Rubidium carbonate was found beneficial in both types of catalysts; thus 100 Ni:18 Mn and 100 Ni:18 ThO₂ catalysts to which rubidium carbonate had been added produced a gasoline yield of 108 ml./m.³ of synthesis gas. Addition of chromium, molybdenum, uranium, and thorium to nickel-manganese catalysts^{22/} demonstrated that, with increase in the atomic weight of the added metal, an increase occurred in promoting action; thorium was determined as the best promoter. Catalysts having the compositions 100 Ni:15 Mn:3 ThO₂ and 100 Ni:50 Mn:3 Al₂O₃ produced gasoline yields of 137 ml. and 130 ml., respectively, per cubic meter of synthesis gas. When 0.5 percent of copper (relative to nickel) was added, virtually no change was produced in the yield of gasoline; as this was increased to 1 percent, the gasoline yield gradually decreased. An optimum copper content of 0.5 percent was thus established.

In 1934, Fujimura and Tsuneoka^{23/} discussed the composition of the products of the synthesis. They found small quantities of acids, alcohols, aldehydes, and ketones in the water formed in the reaction. These investigators also studied the effects of sulfur compounds on nickel catalysts^{24/} and found that whereas a small amount of hydrogen sulfide or carbon disulfide stimulated the catalytic activity of Ni-Mn-Al₂O₃ catalysts and increased the yield of gasoline, these materials were quite harmful to Ni-Mn-ThO₂ catalysts. Studies of the effects of synthesis gas composition^{25/} indicated that 2 H₂:1 CO gas was most suitable. Although excess carbon monoxide had no ill effects on the gasoline synthesis, an excess of hydrogen was found to be deleterious, in that such an excess caused a shift in reaction mechanism from the synthesis of

^{20/} Work cited in footnote 36.

^{21/} Work cited in footnote 31.

^{22/} Work cited in footnote 48.

^{23/} Fujimura, K., and Tsuneoka, S., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure XVII. The General Properties and Chemical Composition of the Reaction Products]: Jour. Soc. Chem. Ind. Japan, vol. 37, 1934, p. 115; supplemental binding pp. 49-51; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 24, 1934, pp. 79-92.

^{24/} Fujimura, K., Tsuneoka, S., and Kawamichi, K., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure XVIII. The Effect of Sulfur Compounds on Nickel Catalysts]: Jour. Soc. Chem. Ind. Japan, vol. 37, 1934, p. 920; Sci. Papers Inst. Phys. Chem. Research (Tokyo); vol. 24, 1934, pp. 93-102.

^{25/} Work cited in footnote 26, p. 15.

gasoline to the synthesis of methane. Watanabe, Morikawa, and Igawa^{26/} of the Central Laboratories of South Manchurian Railway Co., discussed quantitative relationships in the hydrocarbon synthesis. These workers also observed (1) the effects of reaction temperature^{27/} and found that the production of liquid hydrocarbons and water and the gas contraction are similarly affected; (2) the effects of the reduction temperature on activity, and found that for cobalt-copper catalysts 200° to 250° C. was most suitable for reducing the carbonate salts, and 190° to 200° C. was most suitable for reducing the oxides.

Fujimura and Tsuneoka^{28/} observed the effects of the presence of nitrogen, methane, and carbon dioxide in the synthesis gas and found that their only effect was that of a diluent.

Tsuneoka^{29/} studied the relationship between the synthesis gas composition and both the reaction temperature and the degree of product saturation and found that at H₂:CO ratios greater than 2:1, the reaction could be accelerated by increasing the temperature. At H₂:CO ratios less than 2:1, however, the formation of methane could be inhibited by lowering the reaction temperature. The iodine values of the liquid hydrocarbon product indicated that an excess of hydrogen considerably increased the saturation of the product. Tsuneoka also investigated alloy catalysts^{30/} and obtained a gasoline yield of 108 ml./m.³ of synthesis gas by using a catalyst prepared by dissolving out the silicon from a 1 Ni:1 Co:2 Si alloy by means of caustic soda.

Britain

No significant research on the hydrocarbon synthesis has been carried out in Britain.

In 1926-1927, Elvins^{31/32/}, using synthesis gas consisting of 54.6 percent of hydrogen and 44.8 percent of carbon monoxide and employing Co-Cu-Mn

^{26/} Watanabe, S., Morikawa, K., and Igawa, S., [Synthesis of Hydrocarbons by Catalytic Reduction of Carbon Monoxide at Atmospheric Pressure I. Methods of Synthesis and Analysis]: Jour. Soc. Chem. Ind. Japan, vol. 37, 1934, p. 317; supplemental binding pp. 142-146.

^{27/} Work cited in footnote 13, p. 6.

^{28/} Fujimura, K., and Tsuneoka, S., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure XX. Composition of the Initial Gas Mixture]: Jour. Soc. Chem. Ind. Japan, vol. 37, 1934, p. 1543; supplemental binding pp. 704-711; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 25, 1934, pp. 127-136.

^{29/} Tsuneoka, S., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure XXI. Relation of the Gas Composition to the Working Temperature and to the Degree of Saturation of the Products]: Jour. Soc. Chem. Ind. Japan, vol. 37, 1934, p. 1548; supplemental binding pp. 711-716; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 25, 1934, pp. 137-143.

^{30/} Tsuneoka, S., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure XXIII. Efficiency of a New Alloy Catalyst]: Jour. Soc. Chem. Ind. Japan, vol. 37, 1934, p. 1608; supplemental binding pp. 144-151.

^{31/} Work cited in footnote 22, p. 15.

^{32/} Elvins, O., and Nash, A., Synthetic Fuel from Carbon Monoxide and Hydrogen: Fuel in Sci. and Practice, vol. 5, 1926, pp. 263-265.

catalyst (5- to 10-mesh) and at a gas velocity of 6.2 liters per hour with an average reaction temperature of 286° C., obtained from 2.077 cubic meters of synthesis gas, 2.5 gm. of vaselinelike solids, 3.4 gm. of "yellow oil," 1 ml. of water, and 8.15 gm. of insoluble matter. (This corresponds to a yield of 7 gm. of liquid hydrocarbons per cubic meter of synthesis gas.)

In 1928, Erdley and Nash,^{33/} using cobalt and copper catalysts promoted with alumina, zinc oxide, and manganese oxide, found Co-Cu-ZnO to be superior, yielding 7.9 ml. of liquid hydrocarbons per cubic meter of synthesis gas.

The United States

In the United States, as in Britain, no significant research has been carried out on this problem.

In 1928, Smith, Davis, and Reynolds^{34/35/} investigated copper-containing catalysts. According to their results, Co-Cu-U catalyst was most effective and yielded 0.68 ml. of liquid hydrocarbons from 10.7 liters of 1 H₂:1 CO gas at a temperature of 275° C. A detailed study was made of the properties of the hydrocarbons formed with Co:Cu:U catalyst and of the quantity of water gas converted. These investigators found that an excessive temperature was harmful to the catalyst; 18.4 ml. of liquid hydrocarbons was obtained from a liter of water gas by using 2.5 Co₂O₃:0.6 CuO:0.5 MnO catalyst.

France

In 1933, Decarriere and Antheaume^{36/} investigated iron catalyst in the hydrocarbon synthesis. Using 4 Fe:0.1 Cu catalyst, they obtained liquid hydrocarbon yields of 37 gm./m.³ of synthesis gas when the catalyst did not contain potassium carbonate, and when the catalyst did contain potassium carbonate 22 gm./m.³ were obtained. These results contradict Fischer's, which indicate that alkali carbonates exert a promoting effect upon iron-copper catalysts.

In 1934, Antheaume, Decarriere, and Réant^{37/} studied iron-copper catalysts by X-ray analysis and found that the catalyst that had the highest activity consisted almost entirely of Fe₃O₄, with an extremely small amount of Fe₂O₃ present; they found no metallic iron in any case.

^{33/} Work cited in footnote 7, p. 6.

^{34/} Work cited in footnote 10, p. 6.

^{35/} Smith, D. F., Hawk, C. O., and Reynolds, D. A., Synthesis of Higher Hydrocarbons from Water Gas, II: Ind. Eng. Chem., vol. 20, 1928, pp. 1341-1348.

^{36/} Decarriere and Antheaume, J., [An Iron Catalyst for Hydrogenation of Carbon Monoxide at Ordinary Pressures]: Compt. rend., vol. 196, 1933, pp. 1889-1891.

^{37/} Work cited in footnote 81.