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Study on the Formation Mechanism of Methane by Hydrocracking in the Fischer-Tropsch Synthesis

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In the present paper the question has been studied whether the methane formed in great quantities during the hydrogenation of carbon monoxide with hydrogen in the Fischer-Tropsch synthesis may be generated by catalytic hydrocracking of primarily formed higher molecular weight hydrocarbons. The studies were conducted with precipitated Co, Fe, and Ni carrier-type catalysts using ^{14}C labeled compounds.

It has been shown that under normal synthesis conditions with Co and Ni catalysts the percentage of methane formed by catalytical hydrocracking of primarily obtained hydrocarbons related to the total methane formed is only about 5%. The corresponding value for Fe catalysts is below 3%.

Above 204°C with Ni catalysts and above 213°C with Co catalysts noticeable increase of the formation of methane by hydrocracking reactions was observed, the percentage of cracking methane for synthesis with Fe catalysts being largely independent of temperature.

In the hydrogenation of CO with H_2 as performed in the Fischer-Tropsch synthesis (*1*), the quantity of methane deviates from the normal distribution of reaction products plotted as a function of chain length. Therefore it has been assumed by various authors that the formation of methane should be substantially independent from the main reaction proper (*2*). The mechanism of formation of the methane has been discussed in a number of publications (*3*). According to these, there are mainly three versions:

1. Formation by hydrogenation of primarily formed carbides.
2. Formation by hydrogenation of the CO over interfacial, oxygenated, chemisorbed complexes.
3. Formation by hydrocracking of primarily obtained higher molecular weight hydrocarbons.

An experimental investigation on the formation of methane over carbides as an intermediate stage has been conducted by Emmett *et al.* (*4*), using ^{14}C as a tracer in connection with an experimental investigation on the carbide theory for the formation of hydrocarbons in the Fischer-Tropsch synthesis. According to their observations between 8 and 30% of the total methane formed in the synthesis may be formed by hydrogenation of intermediate carbides.

As the formation of methane by hydrocracking of primarily formed higher molecular weight hydrocarbons is well in the range of thermodynamic possibilities (*5*), and furthermore, as our own experimental studies on the hydrogenation of CO with H_2O as performed in the Koelbel-Engelhardt synthesis (*6*) revealed these possibilities, we tried in the present study to determine experimentally the extent of this type of formation mechanism.

For this purpose we proceeded as indicated below. Radioactive hydrocarbons were prepared by Fischer-Tropsch synthesis with a mixture of CO and H_2 to which ^{14}CO had been added. The higher molecular

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weight hydrocarbons were separated and supplied to a second catalyst which had been activated in a synthesis with a nonradioactive CO–H_2 mixture. Having supplied the ^{14}C-labeled hydrocarbons we continued the interrupted synthesis. The methane obtained was separated from the exit gas and analyzed for radioactivity. In this case, the radioactive methane molecules may only have been generated by catalytical hydrocracking of the hydrocarbons supplied, because an isotopic exchange reaction between the higher molecular weight hydrocarbons and the methane could be excluded.

EXPERIMENTAL

The ^{14}CO required for the preparation of the radioactive hydrocarbons, having a specific radioactivity of 1 mC/mmole, was supplied by the Radiochemical Centre, Amersham, England.

The catalysts used for the synthesis as well as for the cracking experiments were prepared as follows:

In the experiments with nickel a carrier type catalyst was used which had been obtained by precipitation of 250 parts by weight of $Ni(NO_3)_2 \cdot 6\ H_2O$, 50 parts by weight of $Mn(NO_3)_2 \cdot 6\ H_2O$, and 34 parts by weight of $Al(NO_3)_3 \cdot 9\ H_2O$ in 600 parts by weight of H_2O adding 60 parts by weight of kieselguhr in a K_2CO_3 solution (210 parts by weight of K_2CO_3 in 600 parts by weight of H_2O) (7).

As iron catalyst a carrier type was used which had been obtained from a hot aqueous $Fe(NO_3)_3$ solution by precipitation with NH_3 and addition of kieselguhr and promoter additives. The catalyst consisted of: 100 parts by weight Fe, 10 parts by weight Mg, 0.5 parts by weight Ca, 0.2 parts by weight alkali (K_2CO_3) and 50 parts by weight of kieselguhr (iron catalyst of Rheinpreussen AG, Homberg).

The experiments with cobalt catalysts were conducted with the commercial cobalt standard catalyst as supplied by the Ruhrchemie AG for the Fischer-Tropsch synthesis. Its composition was:

30.3% by weight Co, 1.48% by weight ThO_2, 2.1% by weight MgO, and 52.1% by weight SiO_2.

Apparatus

The apparatus for the synthesis and cracking experiments consisted essentially of a pressure gas cylinder holding the synthesis feed gas in a ready-to-use ratio, a gas purification train, a flow meter with control devices, a synthesis furnace annex product trap, and a gasometer for the collection of the gaseous synthesis products, Fig. 1.

The storage cylinder for the $^{14}CO/H_2$ mixture was connected with the flow meter and adjusting device by a bypass. In order to maintain the quantity of the radioactive residual gases as low as possible the storage cylinder was dimensioned in such a manner that the glass vessel containing the ^{14}CO had not more space than necessary for destroying by shaking. The gas cylinder was evacuated after attaching the vessel and filled with synthesis feed gas up to the calculated interior pressure which was derived from the flow rate and the desired test period. As, in this case, the gas purification train had to be bypassed with respect to the higher pressure, the pressure gas purifying system tube (see Fig. 1) had been filled with a 30% charcoal and 70% silica gel mixture.

The synthesis reactor was an electrically heated aluminum flat-block furnace with automatic temperature adjustment. The catalyst was filled into a Supremax tube where the catalyst bed was kept in position by two copper spirals. The furnace block had four boreholes parallel to the reaction tube so that the heating jacket of the furnace could be cooled rapidly by blowing in cold air.

The exit gases were separated by fractional desorption from charcoal. The CO and the CO_2 had been removed prior to the adsorption by absorption in a Cu(I)Cl solution, or in KOH, respectively.

The radioactivity of the methane and the other gaseous, liquid, and solid hydrocarbons could be determined only by means of a gas counting tube since the specific radioactivities were in the order of 10^{-10}–

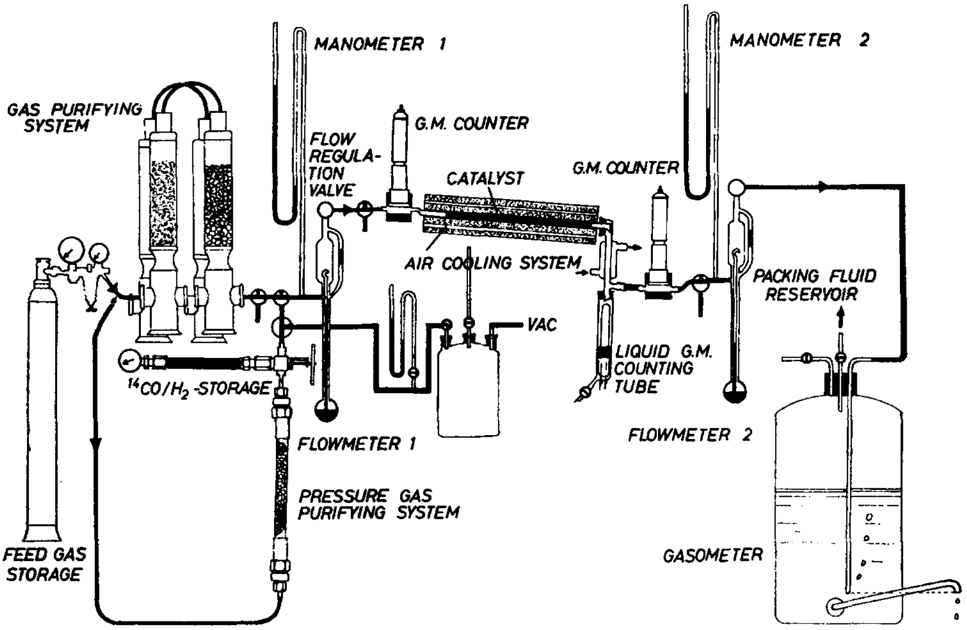

Fig. 1. Apparatus for synthesis and cracking experiments.

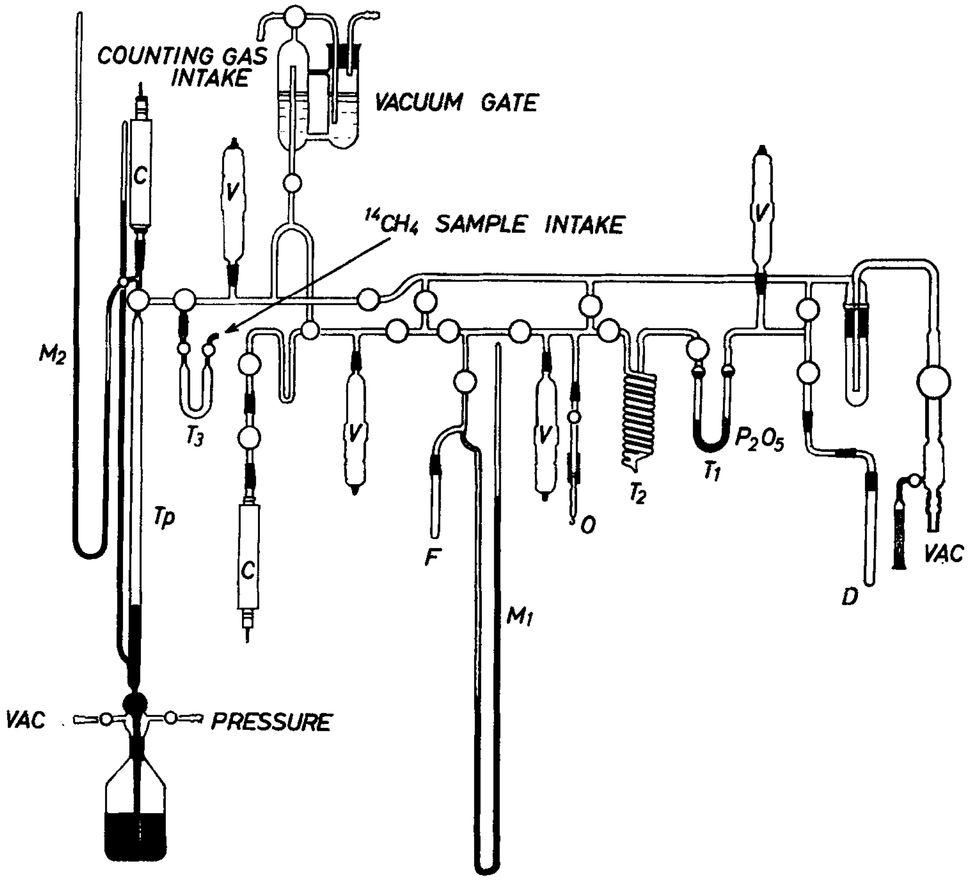

Fig. 2. Vacuum filling apparatus for gas phase counters. C = gas phase counter, D = swivel tube for destroying of the oxidation vessel, F = cool finger, M = manometers, O = oxidation vessel junction, T = traps, Tp = Toepler type pump, V = vacuum gage.

10^{-9} C/ml, and furthermore, since the radioactivities of various hydrocarbons had to be compared reproducibly.

As the radioactivity of methane may be determined without any addition of a counting agent in a gas counter operating in the proportional range, it could be measured directly. In the case of the other hydrocarbons additions of normal methane as counting agents were necessary. The liquid and solid hydrocarbons to be analyzed for radioactivity were burned to CO_2, after which the radioactivity of the CO_2 was determined in a proportional gas counter. For this purpose, the CO_2 was transferred through purification and measuring devices by stepwise condensation with liquid air and subsequent evaporation (see Fig. 2). The water vapor was absorbed by P_2O_5 in trap T_1 while in T_2 the CO_2 was trapped by condensation with liquid air so that the other combustion gases, such as N_2 and O_2, could be pumped off. Having measured the CO_2 volume in M_1 (see Fig. 2) the CO_2 was conducted into the counting tube with methane which served as a counting agent simultaneously.

The gaseous hydrocarbons to be analyzed for radioactivity were pumped from the gas separating apparatus by means of a Toepler type pump passing trap T_3 (condensing the water vapor by Dry Ice) into the proportional gas counter. The Toepler pump served simultaneously as a McLeod manometer so that an exact determination of the volume of the samples analyzed for radioactivity was ensured.

The electrical circuits for the determination of radioactivity by a gas proportional counter are outlined in a block figure, Fig. 3. The electrical circuits consisted of an FZ-35-P gas counting tube (Messrs. Berthold, Wildbad), an FH-524 preamplifier with builtin cathode loper, an inlet adapter, a FH-1/505 precision HV aggregate for 5 kv, and an FH-49 radiation scaler with attached FH-445 time recorder (Messrs. Friesecke & Hoepfner, Erlangen-Bruck).

The plateau length was approximately 300 volts with a slope of 1.6%/100 volts. The plateau was between 3,650 and 3,950 volts. The measuring device was calibrated with $^{14}CO_2$ which had been obtained by oxidation of poly(methyl-^{14}C)methacrylate. The specific radioactivity of the polymer had been established by comparative determination with a ^{14}C standard of the National Bureau of Standards, Washington, D. C. The measuring device for the gaseous hydrocarbons had been calibrated by $^{14}CH_4$ whose specific radioactivity had been determined by combustion to $^{14}CO_2$ which was measured for radioactivity in the calibrated CO_2 apparatus. Accordingly, the counting yield was 71%, the tracing limit 10^{-12} C/ml.

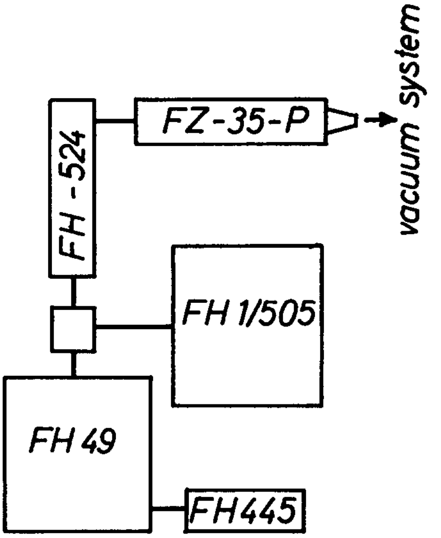

FIG. 3. Electrical circuit for the determination of radioactivity by a gas proportional counter. FZ-35-P, gas counting tube; FH-524, preamplifier with builtin cathode loper; FH-1/505, precision HV aggregate; F-49 radiation scaler with attached FH-445 time recorder.

Procedure

Above all, it had to be considered in the preparation of the radioactive hydrocarbons, that, provided there is a hydrocracking reaction, cracking may already appear during the synthesis of the radioactive hydrocarbons. After extended residence times of the paraffins with the catalyst under synthesis conditions, a substantially cracked hydrocarbon mixture might be left.

Therefore, in the preparation of the radioactive hydrocarbons we had to operate under conditions under which no, or small amounts, only, of methane would be produced. Therefore, the reaction temperatures during synthesis did not exceed 170°C with the Co catalyst, 216°C with the Fe catalyst, and 164°C with the Ni catalyst. Thus, the quantity of methane amounted to 2–4% only, as compared to 15–20% by weight produced under normal synthesis temperatures. Furthermore, after establishment of stationary conditions the synthesis with the ^{14}C-labeled CO/H_2 feed gas was operated for a period of 5 min only, after which the synthesis was interrupted immediately so that the radioactive hydrocarbons formed after switching over to the $^{14}CO/H_2$ mixture were only subjected to synthesis conditions in the catalyst bed for a very short time.

The labeled higher hydrocarbons obtained were extracted from the catalyst with toluene, and the radioactivity of the extracted paraffin waxes was determined. The hydrocarbons were then liquefied under a CO_2 atmosphere and transferred to an activated catalyst which was free from ^{14}C and which already had been used in a normal synthesis test during a running time of 40–45 hr. The catalyst absorbed the hydrocarbons labeled by ^{14}C. Prior to the engagement of the ^{14}C hydrocarbons the paraffin load of this catalyst was between 10 and 20% of the maximum load possible. In order to ensure a good diffusion of the radioactive hydrocarbons into the pores of the catalyst, the catalyst was heated to 75°C for 2 hr with continuous stirring so that a largely homogeneous radioactive phase was obtained, as could be established by secondary tests. In order to simulate the conditions of a normal synthesis and keeping in mind, that during the cracking test, parallel synthesis reaction was continuing to occur, the catalyst was loaded with labeled paraffin waxes prior to the cracking test in such a manner that the full load capacity of the catalyst bed had been reached at the end of the cracking test. The labeled hydrocarbons were in a relation of 6:1 to those formed during the cracking test ensuring that even after extended operation periods the major portion of the paraffin waxes consisted of ^{14}C labeled hydrocarbons.

The cracking tests were conducted at a constant degree of conversion thus eliminating any increase or decrease of the hydrogen partial pressure over the catalyst bed, the influence of the hydrogen concentration on the hydrocracking reaction rate thus being eliminated.

The temperature during the synthesis was increased by 1°C per hour in order to determine the cracking behavior of the paraffin waxes over a large temperature range. In general, the reaction rate was increased with growing temperature so that the space velocity was to be increased in order to maintain the degree of conversion at a constant level. Conversely, the conversion decreased when the reaction temperature was maintained constant for longer periods owing to activity loss by aging, and the space velocity was to be reduced in this case. Thus, while the space velocity during the tests varied between 60 and 90 h^{-1} the CO conversion could be maintained at 95 ± 3%.

The percentage of the hydrocracking reaction related to the entire formation of methane has been calculated from the data of the synthesis and the radioactivity measurements as is outlined below.

The paraffin wax production per unit time could be derived from the material balance by means of continuous exit gas analyses and the determination of the production of liquid hydrocarbons as well as by means of the continuous determination of the CO conversion. Radioactivity measurements in the liquid hydrocarbons revealed that a part of the paraffin waxes—approx. 5% within 30 hr—was removed by the hydrocarbons dripping off the catalyst bed. The hydrocarbons volatilizing off the catalyst were collected in charcoal adsorbers which were arranged in the exit gas flow; their quantity was determined by radioactivity measurements. Furthermore, the total amount of paraffin waxes formed during the cracking test was derived from the difference of the amount of paraffin waxes on the catalyst prior to the cracking test (comprising the produced and the additionally supplied paraffins labeled with ^{14}C) and the total amount of paraffin waxes as determined at the end of the cracking test.

Under the synthesis conditions chosen in these tests the CO conversion to carbide, graphite carbon, and carbonyls was insignificant. Considering all these factors the load of paraffin waxes on the catalyst during a cracking test could be calculated as a function of operation time.

On the other hand, the respective radioactivity of the paraffin waxes could be calculated from the determined radioactivity of the synthesis exit gas and of the liquid hydrocarbons dripping into the product trap, as well as from the radioactivity of the originally supplied ^{14}C paraffins. Thus, the specific radioactivity of the paraffin waxes and their time function was known. Now, by measuring the radioactivity of the methane collected during a certain period of time the weight of carbon which had been converted from the paraffin waxes into the methane during that time could be determined. From this weight, subsequently, the amount of methane which had been formed by hydrocracking of the paraffin waxes could be calculated by the following equation:

$$\frac{{}^{*}CH_4}{CH_4} = \frac{(A_{CH_4}/A_{PW}) \cdot {}^{m}C_{PW} \cdot 133}{{}^{m}CH_4} (\%) \quad (1)$$

where:

${}^{*}CH_4$ = methane formed by hydrocracking, CH_4 = total methane formed

A_{CH_4} = radioactivity (in transmutations per minute) of the methane trapped during time range $t_2 - t_1$

A_{PW} = radioactivity of the paraffin waxes at operation time $(t_1 + t_2)/2$

${}^{m}C_{PW}$ = amount of carbon (in mg) as paraffin waxes at operation time $(t_1 + t_2)/2$

${}^{m}CH_4$ = amount of total methane (in mg) formed in time range $t_2 - t_1$

As the catalyst load with ^{14}C labeled paraffin waxes was always equal both with regard to the extent of loading for all tests and in view of the effective amounts of paraffin waxes for tests at the same catalyst, the data obtained from the various cracking tests could be compared. The extent of loading at the beginning of each cracking test was 80–85% of the maximum load.

RESULTS AND DISCUSSION

Prior to the cracking tests we studied the influence of isotopic exchange reaction between the higher molecular weight hydrocarbons and methane in a preliminary test. For this purpose, radioactive paraffin waxes were loaded on charcoal, after which a gas mixture containing inactive methane was conducted over the loaded charcoal under synthesis conditions, and we determined the radioactivity in the methane. The gas mixture had the same composition as that formed during the cracking tests over the catalyst bed. As may be derived from the radioactivity data in the methane compared to those determined during the cracking tests, the percentage of radioactivity in the methane owing to an isotopic exchange was between 1 and 5% of the total methane radioactivity only.

In another preliminary test the question had to be settled whether—after the beginning of the cracking reaction—the crackable fractions of the ^{14}C labeled paraffin waxes might perhaps be cracked completely and so rapidly that after a short period of time no radioactivity could be traced any more in the exit gas or methane, respectively, although the newly formed inactive paraffin waxes will generate further, but inactive methane. For this purpose, we observed the radioactivity in the methane for an operation time of 16 hr at a constant temperature of 176°C and found the radioactivity in the methane to be reduced to about one-half of the initial value within 7 hr. As in the subsequent cracking tests the operation times were between 24 and 36 hr the influence of the decrease of radioactivity with time in the methane was not too serious. It could also be shown by this test that in the preparation of the ^{14}C labeled paraffin waxes any cracking to methane was practically excluded as the ^{14}C paraffins had residence times of max. 5–8 min, only, under synthesis conditions at the catalyst after their preparation.

As the evaluation of the cracking tests with a Co catalyst showed, the percentage of the methane formed by hydrocracking of the paraffin waxes as calculated from Eq. (1) at temperatures between 180° and 200°C and with a H_2/CO feed gas ratio of 2:1 amounted to approximately 2% of the total amount of methane formed in the synthesis (Fig. 4). Above 213–214°C an increase of the hydrocracking reaction up to two- to fourfold was observed, which, however, appears to be restricted to certain crackable fractions of the paraffin waxes. Exact statements on the behavior above 213°C cannot be given since the decrease of the radioactivity in the methane owing to a consumption of the crackable ^{14}C labeled paraffin waxes became too extensive. The increase of the CO conversion to CH_4 to be observed above 192–193°C—as calculated from the equation:

$$\frac{\mathrm{CH_4}}{\mathrm{C_{1^+}}} = \frac{V_{\mathrm{CH_4}}{}^{\mathrm{E}} \cdot (1 - k) \cdot 100}{V_{\mathrm{CO}}{}^{\mathrm{F}} - (V_{\mathrm{CO}}{}^{\mathrm{E}} + V_{\mathrm{CO_2}}{}^{\mathrm{E}})(1 - k)} \ (\%) \qquad (2)$$

($V_x{}^F$ = vol % of component x in the feed gas; $V_x{}^E$ = vol % of component x in the exit gas; k = contraction factor, C_{1^+} total amount of hydrocarbons formed) and also shown in Fig. 4—is in no obvious way connected with the increase of methane formed by hydrocracking.

An increase of the hydrogen partial pressure by only 10% at temperatures between 180° and 200°C caused the percentage of methane formed by hydrocracking to increase two- to fourfold (Fig. 5). The data calculated from Eq. (1) and given in the diagrams are likely to be lower than the real synthesis values, because in the temperature range between 180° and 213°C, the decrease of radioactivity in the methane owing to a consumption of the crackable ^{14}C paraffin wax fractions already became noticeable and hence has to be taken into consideration. The approximate factor for this correction in the temperature range between 180° and

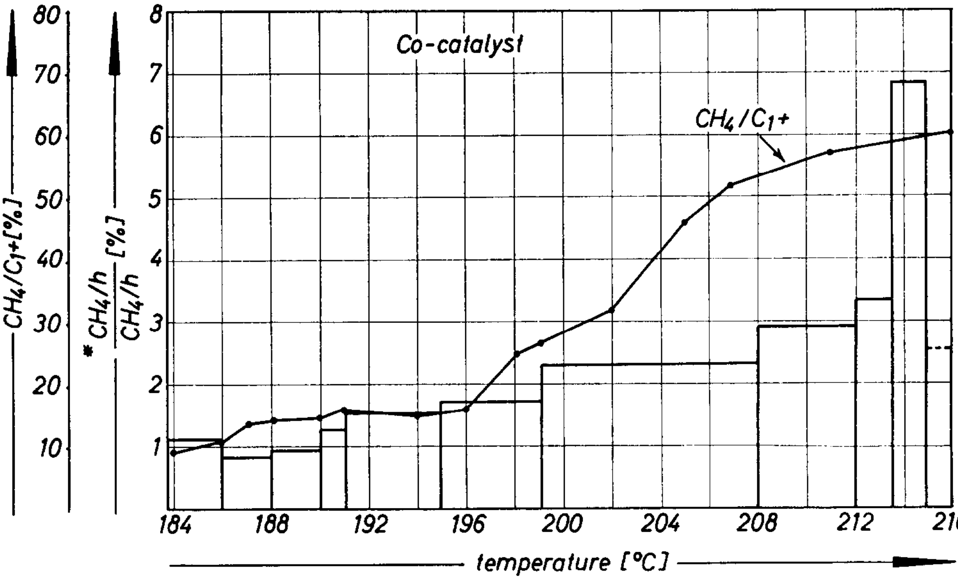

FIG. 4. Percentage of methane formed by hydrocracking of paraffin waxes $^*CH_4$ related to the total methane (CH_4 formed in the synthesis with Co catalyst and percentage of CO conversion into methane related to CO conversion into hydrocarbons, total (C_1^+) as functions of temperature. Pressure, 1 atm; CO conversion, 95 ± 3%; feed gas ratio CO/H_2 = 1:2.

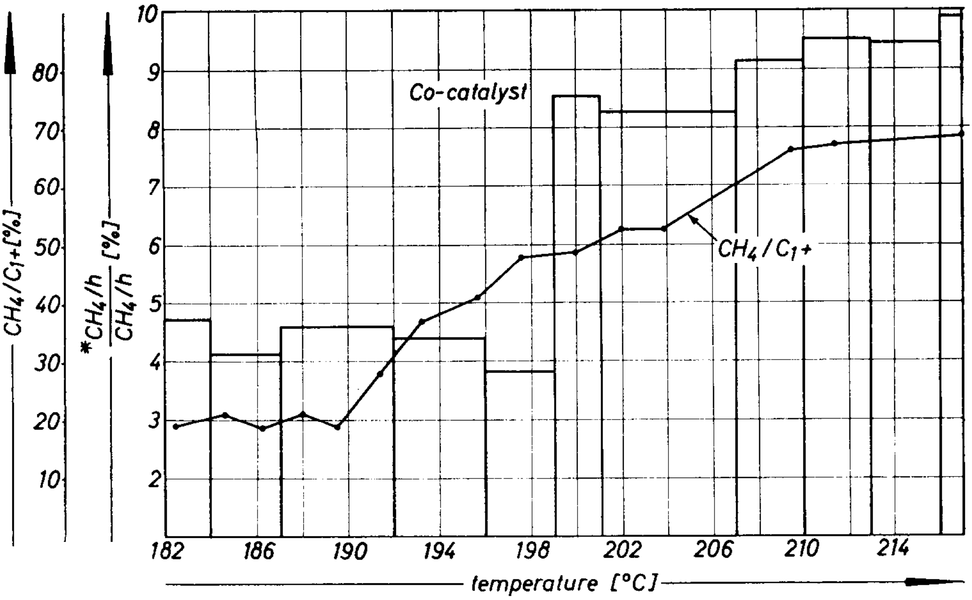

FIG. 5. As in Fig. 4, but feed gas ratio $CO/H_2 = 1{:}3$.

200°C was determined by an experiment in which the ^{14}C paraffins were supplied not at 180°C but at 198°C. From this experiment we may conclude, that the amount of hydrocracking will be about 100% higher than suggested by the data calculated from Eq. (1).

Therefore, it may be stated with some confidence that the percentage of methane formed by hydrocracking during synthesis with the Co catalyst used under the conditions stated and for temperatures between 180° and 200°C, and a feed gas ratio of $H_2/CO = 2{:}1$ will not exceed 5% of the total amount of methane formed.

The percentage of methane formed by hydrocracking for synthesis with Fe catalysts is lower than the corresponding value in the synthesis with Co catalysts (Fig. 6). The percentage is below 3% related to the total CH_4 formed in the synthesis. Even at temperatures above 300°C no increase beyond this value could be observed.

The behavior is quite different in the synthesis with Ni catalysts. The percentage of the cracking reaction for the forma-

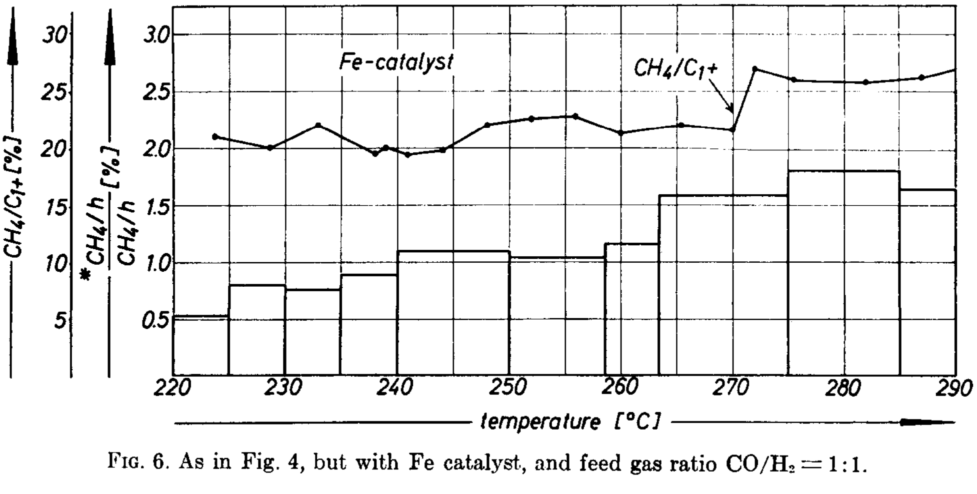

FIG. 6. As in Fig. 4, but with Fe catalyst, and feed gas ratio $CO/H_2 = 1{:}1$.

tion of methane at temperatures between 180° and 200°C was approximately 4%. Beyond 204°C the percentage of the methane formation owing to the hydrocracking is steadily increasing with increasing temperature. At 240°C the percentage of the hydrocracking reaction has been increased up to 7–8%. As, for the range in question, the decrease of radioactivity in the methane owing to the consumption of the crackable ^{14}C paraffin wax fractions is only about $1/_{10}$ of the corresponding value for synthesis at Co catalysts, it may be concluded that the quantity of the paraffin waxes being hydrocracked with the Ni catalyst—at least at higher temperatures—is considerably higher than that with the Co catalyst (Fig. 7). As may be derived from Fig. 7 the increase of the CO conversion to methane related to the total hydrocarbons formed as calculated from Eq. (2) is in a certain relation to the increase of the formation of methane from hydrocracking reaction proper.

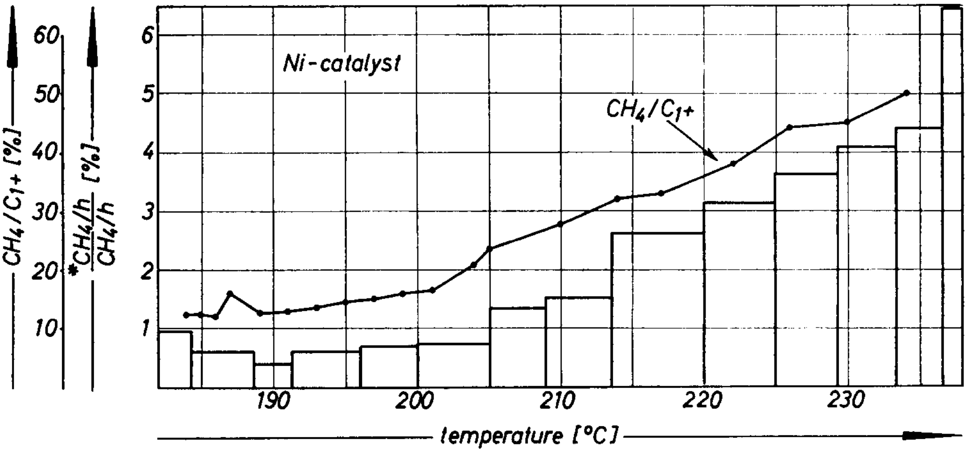

FIG. 7. As in Fig. 4, but with Ni catalyst, and feed gas ratio $CO/H_2 = 1:2$.

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