ents. No deterioration has been observed even after repeated use, although, if the zinc sulfide fluorescence is to be utilized, care must be exercised to ensure that the zinc sulfide particles remain uniformly dispersed. The recovered material is a distinctly weaker adsorbent than fresh silicic acid and minor variations have been noted in the strength of various recovered batches. The weaker adsorptive properties of the recovered silicic acid have been an advantage in the present work, since they permitted several separations which could not be attained on fresh silica gel.

Acknowledgment.—The author would like to express his appreciation to Mary L. Sease who assisted in carrying out the experiments, and to Dr. Frank Swindells and Dr. Emery Meschter of the Photo Products Department of the du Pont Co. for their kindness in making available the fluorescent materials used in this work.

Experimental

Silicic acid (Merck Reagent, diluted with 50% Celite 535, or Eimer and Amend, C. P., undiluted) was mixed thoroughly with 2.5% of No. 62 zinc sulfide[4] and 2.5% of No. 609 zinc silicate[4] and packed in a quartz chromatographic tube of 2.2 cm. inner diameter; 5–10 ml. of petroleum ether (Skellysolve F, b. p. 35–60°) solution containing the two substances to be separated was poured on the column, which was then developed with petroleum ether containing 0–20% of USP diethyl ether. Movement of the zones was observed by illuminating the column in a darkened room with ultraviolet light from a hydrogen lamp detached from a Beckman Spectrophotometer.

At the conclusion of development each shadowed zone was isolated mechanically and dried in the air for one-half to twelve hours. Elution with 50–75 ml. of 96% ethanol gave a solution whose qualitative and quantitative composition could easily be determined on a Beckman Spectrophotometer. In those experiments where no apparent separation had occurred, the top and bottom thirds of the shadowed zone were separated, eluted with alcohol and analyzed spectroscopically, the middle third being discarded. In the one case where the two separated compounds had the same spectral absorption (dimethyl phthalate and dibutyl phthalate) the zones were eluted with 30–40 ml. of diethyl ether, the ether was evaporated off, and the residue, after purification by fractional distillation according to the technique of Morton and Mahoney,[5] was identified by its boiling point.

Fresh adsorbent was prepared for use and used adsorbent was recovered by washing in a large chromatographic tube with $3V$ of 96% ethanol (V is that volume of liquid required to wet the silicic acid[6]), next with $1V$ of diethyl ether, and finally with $3V$ of petroleum ether. The extruded adsorbent was dried for a few minutes in the air and then for at least eight hours in a desiccator evacuated continuously by a mechanical oil pump.

Summary

A mixture of silica gel with fluorescent zinc silicate and zinc sulfide has been found to be much superior to the silica gel–zinc sulfide mixture used in earlier work on the chromatography of colorless compounds, from the standpoint of both ease of visibility and number of compounds visible. Forty separations involving twenty-five compounds are described and adsorption sequences are given.

MIDDLETOWN, CONN. RECEIVED JUNE 16, 1948

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[4] Obtained from the Photo Products Division, E. I. du Pont de Nemours and Co., Inc., Towanda, Penna.

[5] A. A. Morton and J. F. Mahoney, *Ind. Eng. Chem., Anal. Ed.* **13**, 494 (1941).

[6] W. A. Schroeder, *Ann. N. Y. Acad. Sci.*, **XLIX**, 204 (1948).

[CONTRIBUTION FROM GULF RESEARCH & DEVELOPMENT COMPANY'S MULTIPLE FELLOWSHIP, MELLON INSTITUTE]

Some Mechanism Studies on the Fischer–Tropsch Synthesis Using C^{14}

BY J. T. KUMMER, T. W. DEWITT AND P. H. EMMETT

Fischer[1] and his co-workers have suggested that the metallic carbide is an intermediate in the synthesis of hydrocarbons from carbon monoxide and hydrogen over the catalysts iron, nickel and cobalt. This theory has also been accepted by numerous later writers. The use of the recently available radioactive carbon isotope, C^{14}, as a tracer seemed to provide a possible direct method for testing this hypothesis. Accordingly, the experiments described in this paper were undertaken. We have attempted to determine whether the mechanism of hydrocarbon synthesis over iron and cobalt catalysts is the formation of a carbide by the reaction of carbon monoxide with the metal catalyst followed by the reduction of the surface of this carbide to methylene groups which combine to form hydrocarbons; or whether, on the other hand, the mechanism is such that the hydrocarbons are formed by some adsorption mechanism that does not involve the carbide as an intermediate.

The general plan of the experiments was quite simple. If the carbide is an intermediate, a surface layer of metal carbide containing radioactive C^{14} should cause the initial hydrocarbon products formed by exposing a mixture of hydrogen and normal carbon monoxide to the radioactive carbide at synthesis conditions to be approximately as radioactive as the surface. Similarly, a surface carbided with non-radioactive carbon monoxide should, on contact with a H_2–$C^{14}O$ mixture, at first form hydrocarbons with much lower radioactivity than that of the H_2–$C^{14}O$ mixture. Before the synthesis experiments could be carried out, however, it was necessary to prepare a surface containing C^{14} as metal carbide, and to determine whether the *exchange* of the carbon in carbon monoxide and in other hydrocarbons with the carbon

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[1] Fischer and Tropsch, *Ges. Abhandl. Kenntnis Kohle*, **10**, 313 (1932).

of the metal carbide at synthesis temperatures was going to be so fast as to render the interpretation of the synthesis experiments very difficult or impossible.

Experimental

Materials.—The C^{14} used in these experiments was obtained as barium carbonate from Dr. John Dunning of Columbia University and was prepared by use of a cyclotron. Radioactive carbon monoxide was made by driving off carbon dioxide with phosphoric acid from a small amount of the barium carbonate, and then exchanging the carbon in this small amount of highly radioactive carbon dioxide (0.2 cc.) with the carbon in several hundred cc. of carbon monoxide over a hot tungsten filament, as recently described,[2] to give carbon monoxide of suitable activity for our experiments ($\sim 10^5$ disintegrations per minute per cc.).

The carbon monoxide was prepared by the action of phosphoric acid on formic acid at 180° and was passed in succession over soda lime, hot copper (200°), more soda lime, and finally through a Dry Ice trap into a storage bulb.

The carbon monoxide–hydrogen mixtures used in the few flow experiments were made by mixing tank carbon monoxide and tank hydrogen in the desired proportions in a metal cylinder.

Four different types of catalysts designated as A, B, C and D, all of 8–14 mesh size, were used in these experiments though most of the runs were made over catalyst B. Catalyst A was a fused pure iron oxide synthetic ammonia catalyst approximating Fe_3O_4 in composition. Catalyst B was a promoted, fused, synthetic ammonia catalyst containing 2.26% aluminum oxide, 0.62% silicon dioxide and 0.21% zirconium oxide as promoters. Carbon monoxide chemisorption experiments indicated that 35% of the surface of catalyst B was iron, and 65% was promoter. Catalyst C was a standard cobalt–thoria–Kieselguhr catalyst (100:18:100) of the type used by British Fuels Research. Catalyst D was iron oxide precipitated from ferric nitrate solution by sodium carbonate at 100°.

Apparatus and Procedure.—All samples to be counted were burned to carbon dioxide, precipitated as barium carbonate, and counted with a thin window, bell-shaped Geiger counter obtained from Dr. John Dunning. The counting technique used was that described by Reid.[3] The high voltage supply and scaling unit (Model BS-4) was manufactured by Technical Associates. The tube background was 20 counts per minute.

The combustion and precipitation were carried out in the apparatus shown in Fig. 1. The gas sample was burned in oxygen over a heated platinum filament in pipet A. The carbon dioxide was trapped in the finger of A cooled in liquid nitrogen, and the excess oxygen was evacuated. The carbon dioxide was then measured in the gas buret shown in Fig. 2 while the finger of A was kept in Dry Ice. The volume of carbon dioxide was adjusted to a standard size by either evacuating some of the gas or by adding a known amount of normal carbon dioxide and mixing. Finally, this sample of carbon dioxide was condensed with liquid nitrogen in trap B. The stopcock D was then opened to the hydrogen line with the trap B still in liquid nitrogen; stopcock E was opened full and the hydrogen flow regulated by D to about a bubble per second through the barium hydroxide solution. The liquid nitrogen trap was next removed from B and the carbon dioxide flushed into the barium hydroxide solution and precipitated as barium carbonate in C. The solution in C was sucked out by a water aspirator through a filter paper (~2 cm. diameter) which, in turn, could be removed by means of a piece of bent wire that lay partially under and projected up through the center of the paper. This sample was mounted on a one-inch Newman cap and counted in a standard position. The standard size sample for counting was precipitated from 1.3 cc. of carbon dioxide. Since the sample sizes varied somewhat around the value 1.3 cc., all sample activities were corrected[3] for self absorption.

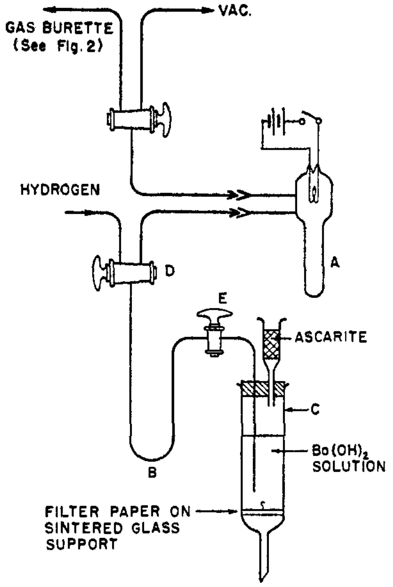

Fig. 1.

The apparatus in which all the experiments were carried out is shown in Fig. 2. The catalyst (2–3 g.) in the sample bulb A was reduced in a hydrogen stream with a space velocity of 2,000, volumes of gas per volume of catalyst per hour and at temperatures up to 400° for catalyst A, up to 500° for catalyst B, and up to 430° for catalyst C. Catalyst D was not reduced in hydrogen. The reduction took about three days and was continued until no water could be visually detected in trap B (Fig. 1) after the exit hydrogen stream from the sample had passed through the trap in liquid air for fifteen minutes.

After being evacuated at the final reduction temperature, the sample was carbided by a measured amount of carbon monoxide in the buret bulbs being circulated over the sample at 200–270° and through the trap F in liquid nitrogen to remove the carbon dioxide. By measuring the amount of carbon monoxide consumed and carbon dioxide produced (a small amount, about 0.3%, of oxide is always formed during carbiding) it is possible to find the amount of carbon on the sample as the carbide Fe_2C.[4] The sample was evacuated after carbiding.

For synthesis, a mixture of hydrogen and carbon monoxide was made up in the buret bulbs, mixed, and circulated over the sample as during carbiding. The pressure during synthesis was kept constant by raising the mercury in the buret bulb as the gas was consumed until the mercury reached the top of the gas buret. If synthesis was carried past this point, the pressure dropped. The part of the apparatus in Fig. 2 to the left of stopcock E held about 0.1 cc. (S.T.P.) of gas per mm. of pressure, and the buret bulbs when empty of mercury held 0.27 cc. (S.T.P.) of gas per mm. of pressure. All products of the reaction except 11 mm. of methane (the v. p. at −195°) were removed in the liquid nitrogen trap F. After synthesis, the gas phase was analyzed for its three components, methane, carbon monoxide and hydrogen, by combustion in oxygen. While taking the gas phase sample for analysis, care was taken to warm the trap slightly (to about −175°) so that any solid methane that may have been in it would vaporize into the sample. For runs in which the radioactive count of both the carbon monoxide and methane was deter-

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(2) Kummer, This Journal, 69, 2239 (1947).

(3) D. W. Wilson and others, "Preparation and Measurements of Isotopic Tracers." Edwards Brothers, Inc., Ann Arbor, Michigan, 1946.

(4) We have identified this phase by X-rays as that referred to in the literature (K. H. Jack, *Nature*, **158**, 60 (1946)), as $Fe_{20}C_9$. For simplicity, however, we shall continue to call it Fe_2C.

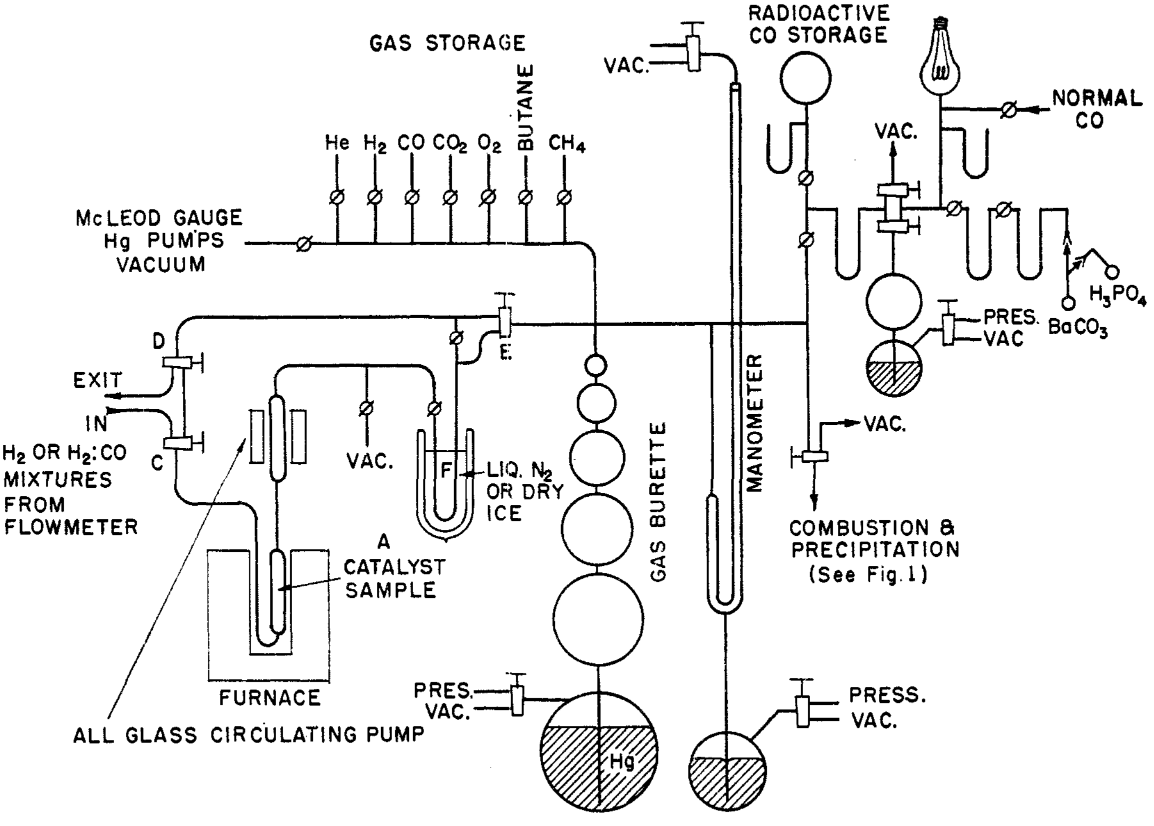

Fig. 2.

mined, a slightly modified procedure was used. With liquid nitrogen around trap A (Fig. 2) the gas phase was first transferred to the combustion pipet A (Fig. 1) by using the gas buret (Fig. 2) as a Toepler pump. This sample contained most of the carbon monoxide but very little methane (only that due to the 11-mm. vapor pressure of methane in trap A). This sample was then analyzed for carbon monoxide, methane and hydrogen by combustion in the usual way and the carbon dioxide formed was counted for its radioactive content. Next, a methane-rich sample was obtained by warming trap A to about −150°. This sample containing mostly methane together with small amounts of carbon monoxide and hydrogen from the connecting tubes was analyzed for carbon monoxide, hydrogen and methane in the combustion pipet and the carbon dioxide was counted. From these two analyses, the total amount of hydrogen, carbon monoxide and methane could be calculated together with the radioactivity of the carbon monoxide and methane. After this analysis, trap F (Fig. 2) was evacuated at −195° and then warmed to −78° while open to the combustion pipet A (Fig. 1) which was cooled in liquid nitrogen. This collected the material from Trap F with a vapor pressure greater than 0.1 mm. at −78°. This material in the combustion pipet was volatilized by warming to room temperature, measured, freed of carbon dioxide by passage over ascarite and burned in oxygen to find its average molecular weight and C:H ratio. (This was called gasol fraction.)

The material remaining in trap F was then analyzed for water and other hydrocarbons (called liquid fraction); these latter were reported as cc. of carbon dioxide produced by combustion. The carbon dioxide from all combustion analysis was precipitated and its radioactivity measured.

In a few synthesis experiments, a flow system was used by admitting a premixed hydrogen–carbon monoxide gas through stopcock C, and passing it over the sample, through a trap cooled in liquid nitrogen and out stopcock D. At the end of each flow run the hydrocarbons from the trap were removed and analyzed as described above.

All catalyst surface areas were obtained from B.E.T. plots of nitrogen adsorption isotherms; the amount of carbon monoxide chemisorbed by the catalysts at −78.5° was determined by direct measurement in the usual way.[5] These chemisorption measurements were needed to determine the amount of free metal surface on the catalysts and to obtain, thereby, an estimate of the amount of carbide carbon that a catalyst surface might hold. The assumption was made that each iron atom of the reduced and uncarbided sample chemisorbed a molecule of carbon monoxide, and that on the carbided sample there was one-half this number of carbon atoms associated with the surface as Fe_2C. In this paper we shall, for convenience, speak of cubic centimeters of carbon equivalent to the surface carbon of the catalyst instead of the number of moles of carbon; we shall mean the cc. that would result if the surface carbon were a perfect gas of atomic carbon or if it were converted to methane.

Results and Discussion

Surface Area of the Catalysts.—The total free metal surfaces of catalysts B and C are shown in column 3, Table VI. Runs 3 S to 14 S were made on a 1.89-g. sample of catalyst B whose total area was not measured; runs 22 S to 26 S were made on a 2.24-g. sample having an area of 25.2 sq. m. per gram; runs 27 S to 31 S were made on a 30-g. sample of catalyst B having an area of 16.6 sq. m. per gram. On all samples of B, about 35% of the surface was free iron[5]; the remainder was apparently covered by promoter.

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(5) Emmett and Brunauer, This Journal, 59, 1553 (1937).

TABLE I

KINETIC DATA FOR CARBIDING IRON WITH RADIOACTIVE CARBON MONOXIDE

No.	Experiment	Temp. of carbiding, °C.	% Fe$_2$C in run Before	% Fe$_2$C in run After	Temp. of run, °C.[a]	Methane sample, cc.	C_s^0 c/min./cc.	C_s c/min./cc.	C_g c/min./cc.	Q, cc.	N_s Calcd. from eqn., 1 or 2 cc.	N_s from chemisorption, cc.
1c	Carbiding Fe$_2$C*[b] of catalyst A with normal CO	325–9 cc. 225–12.2 cc.	10.7	16.0	225	0.61	1640	255	0	21.2	11.5	0.30
2c	Carbiding Fe$_2$C of catalyst B with C*O	250	58.6	60.9	250	0.71	0	415	1640	9.07	32.4	2.0
3c	Recarbiding above sample with CO	250	60.9	62.2	250	0.78	384	183	0	5.1	6.8	2.0
4c	Carbiding Fe$_2$C of catalyst B with C*O	250	58.0	61.0	250	0.076	0	910	2660	11.7	28.0	2.0
5c	Carbiding Fe$_2$C* of catalyst B with C*O	265	~76.9	80.3	265	0.25	177	1375	2660	13.3	20.2	2.0
6c	Carbiding Fe$_2$C* of catalyst B with C*O	252	~84.1	87.6	260	0.20	388	1088	3420	13.9	46.0	2.0
7c	Carbiding Fe$_2$C* of catalyst B with C*O	265	~93.5	94.7	250	0.75	535	1410	3500	4.8	13.7	2.0
8c	Carbiding Co$_2$C of catalyst C with C*O	200–230	69% Co$_2$C	76.3	234	1.5	0	659	2700	11.1	40.0	2.2
9c	Carbiding Fe$_2$C of catalyst B with C*O	225–246	63.2	65.7	250	0.31	0	602	2590	11.5	43.3	2.32
10c	Carbiding Fe$_2$C of catalyst B with C*O	200–250	63.6	65.5	250	0.22	0	524	3190	8.7	47.8	2.32
11c	Carbiding Fe$_2$C of catalyst B with C*O after 9.08 cc. of carbon were removed by H$_2$	200–243	65	66.1	250	0.42	0	2040	5120	10.13	20	2.32

[a] Temperature at which surface was reduced by hydrogen to give methane for surface activity. [b] C* is used throughout this table as a symbol for C^{14}.

The differences between the surface areas of two of the separate samples of catalyst B are probably to be attributed to slight differences in the space velocity and temperature schedule of the reduction. Cobalt catalyst C used in runs 15 S and 16 S was not measured with nitrogen since only the chemisorption of carbon monoxide seemed to be needed for interpreting the synthesis results.

Catalyst A, as shown in Table I, had a total carbon monoxide chemisorption of about 0.6 cc. for the 1.97 g. sample. This is in approximate agreement with surface area values obtained from nitrogen isotherms on other portions of this same catalyst (~ 1.3 sq. m./g.).

Catalyst D, the precipitated ferric oxide sample, had a surface area of 168 sq. m. per gram before use and 57.8 sq. m./g. after use. The carbon monoxide chemisorption value was not taken since the catalyst was merely pretreated with carbon monoxide at 325° before use but was at no time reduced completely to metallic iron.

Carbiding Iron with Carbon Monoxide.—These experiments were made to ascertain whether or not a time-stable radioactive surface could be made with economical use of C^{14} and, as a secondary result, to obtain information about the mechanism of carbiding. The first experiments were performed by partially carbiding the reduced sample with normal carbon monoxide, carbiding a little further with a small amount of radioactive carbon monoxide and then measuring the concentration of radioactive carbon on the surface. This surface radioactivity was measured by reducing a small fraction (~$^1/_4$) of the surface with hydrogen to form methane, burning the methane to carbon dioxide, precipitating this as barium carbonate and counting. The activity of the surface can then be expressed as counts per minute per cc. of methane, which would be equivalent to counts per minute per cc. of surface carbon. The results of the carbiding experiments are shown in Table I.

Column 9 in Table I shows the radioactive count of the surface carbon at the end of each carbiding experiment. It is evidently possible by the methods here used to build up a layer of radioactive carbide. However, a comparison of columns 9 and 10 shows that the final radioactivity of the surface (column 9) is always much less than that of the radioactive gas (column 10) used in carbiding in spite of the fact that the total quantity of carbon, Q, (expressed as cc. of carbon or methane) put on (column 11) during the carbiding with radioactive carbon monoxide was two to seven times as great as the amount of carbon believed necessary to form a simple layer of surface Fe$_2$C (column 13).[6] Even in run 11c in which the equivalent of about four layers of surface carbide was removed by reduction with hydrogen immediately before the carbiding, the final surface activity was much smaller than that of the gas used for the radioactive carbiding.

A more quantitative evidence of the slowness with which the radioactivity of the surface builds up can be obtained by setting up a possible equation for the rate of carbiding. If the surface carbided uniformly and if it is viewed as containing a large constant number of carbon atoms such that one atom moves into the interior as each new carbon atom from the reacting carbon monoxide enters the surface (the surface, thereby, being continually and uniformly diluted with reacting gas) then the change in surface activity would be given by

$$\frac{dC_s}{dt} = (C_g - C_s)\frac{1}{N_s}\frac{dQ}{dt} \qquad (1)$$

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[6] The question naturally arises as to whether the carbon dioxide formed by the carbiding process possesses the same radioactivity as the carbon monoxide being used for carbiding. This was checked in only two carbiding experiments. The activities of the two carbon dioxide samples were found to be 3440 and 2510 when the carbon monoxide had activities of 3500 and 2700 counts per minute per cc., respectively. These carbon dioxide activities were considered to be the same as those of the carbon monoxide within experimental error.

which on integration gives

$$C_s = C_g - (C_g - C_s^0)e^{-Q/N_0} \qquad (2)$$

where t is time; C_s^0 is the initial surface activity in counts per minute per cc. of surface carbon; C_s is the surface activity at time t; C_g is the activity of the carbiding gas; Q is the total number of cc. of carbon going to form carbide during the run; and N_0 is the total number of cc. of carbon (CH_4) equivalent to the surface. Experimental values for C_s^0, C_s, C_g and Q are given in columns 8, 9, 10 and 11 of Table I. By inserting these values into equation 2, one can calculate the value of N_0 that would exist if equation 2 were followed. As is evident, N_0 calculated from equation 2 (column 12) is much larger than the N_0 obtained by chemisorption measurements. Another way of stating this is to point out that the surface activity does not change as rapidly with carbiding as one would expect from equation 2. This study, however, was not sufficiently extensive really to test this form of the carbiding law so it is not possible to say with certainty whether the high N_0 values calculated by equation 2 reflect a participating surface larger than that measured by adsorption or whether it merely indicates that the law is not obeyed.

Even in run 11c in which, as mentioned above, the equivalent of four layers of iron carbide were removed immediately before carbiding with $C^{14}O$, the calculated N_0 value is still about nine times as large as the measured value for N_0. It is apparent that the building up of C^{14} concentration is still much too sluggish even in this run. If the carbon was removed uniformly from the surface by the preliminary reduction, then it must have been partially replaced by carbon from underlying layers; otherwise, the radioactive carbon monoxide would have reacted with this free iron to give a surface of an activity equal to the gas activity. The possibility, of course, still remains that carbon is not uniformly removed from the surface by reduction.

Several experiments were conducted to see whether a radioactive surface, once formed, changed appreciably with time. The four experiments of Table II show that the surface concentration of C^{14} as measured by reduction with hydrogen changes only slowly[7] with time, and that such a change does not constitute a serious complicating factor in synthesis studies.

In the hope of finding an explanation of why a carbided sample always has a lower surface radioactivity than that for a similar amount of carbon in the radioactive carbon monoxide used for carbiding, the sample, after run 11c, Table I, was reduced in successive steps at 253° to 300°, and the radioactivity of each sample of methane formed in this reduction was measured. Table III shows the results and Fig. 3 shows a plot of total counts removed against total cc. removed. This distribution does not necessarily represent the distribution immediately after carbiding since, during the twenty-three days required for the run, the distribution may have changed. Although the time studies in Table II indicated no serious change in a matter of a number of hours, they did not cover periods as long as twenty-three days. It is also possible that the results may have been somewhat modified by the experimental technique. During each reduction, part of the methane produced was circulated over the sample with hydrogen and this, by virtue of the fact that methane can carbide iron, may have caused redistribution of the C^{14}. However, it is known that the rate of carbiding by methane at this temperature is extremely slow so that probably the result cannot be attributed to the small amount of circulating C^{14}.

Table II

Change of Surface Activity with Time

Experiment	Fe_2C %	Temp., °C.	Surface activity at indicated elapsed time in hours						Activity[a] value at equilibrium
			0	24	48	51	67	91	
1t	61	250	663	419	...	...	412	388	61
2t	80	300	565	685	589	590	...	...	98
3t	80	305	755	...	665	...	...	...	98
4t	62	325	183	175	...	...	...	...	60

[a] This column is the activity per minute per cc. of carbon dioxide if the C^{14} atoms were distributed uniformly throughout the carbide.

Table III

Stepwise Reduction of Sample 11c[a]

Time, hours	Temperature of reduction, °C.	CH_4 produced in each step, cc.	Counts per min. per cc. CH_4	Total of CH_4 produced, cc.	Total counts per minute taken off sample
0	253	0.0	..	0	0
2	253	0.58	2040	0.58	1185
28	253	1.38	1430	1.95	3155
72	272	2.11	1042	4.06	5355
130	300	2.00	773	6.06	6905
170	300	1.96	825	8.02	8523
190	300	2,59	574	10.61	10008
220	300	3.13	615	13.74	11933
310	300	2.94	559	16.68	13575
340	300	2.75	490	19.43	14925
360	300	18.72	388	38.15	22185
380	300	18.30	306	56.45	27785
450	300	14,25	211	70.70	30785
500	300	120.00	97	190.7	42435
520	300	106.5	68	297,2	49695
570	300	11.0 Completely reduced	83	308.2	50608

[a] The sample consisted of 2.285 g. of iron catalyst B previously carbided to 66.1% conversion to Fe_2C. This carbon content is equivalent to 300 cc. of CH_4. The CO chemisorption on the sample at −78° was 4.64 cc.; it is, therefore, assumed that the carbon in the surface carbide is equivalent to 2.32 cc. of CH_4. The total radioactive carbon in the sample had 52,000 counts per minute. The total count was determined by measuring the total amount of carbon monoxide disappearing and subtracting the total amount of carbon dioxide formed.

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(7) Apparently one of the first two observations in run 2t involves a reading error in counting. In all other runs, the first reading was slightly larger than those made at later periods.

From these carbiding results it is evident that the simple carbiding picture of a uniformly reacting surface represented by equations (1) and (2) is not adequate and that the carbiding is rather complex. One might explain the failure of equations (1) and (2) by saying that the increase in C^{14} on the surface while carbiding with radioactive carbon monoxide was slower than expected by virtue of the reaction occurring only at active points or by virtue of much of the surface being in the form of crystallites of iron so small as to be completely converted to Fe_2C in the initial treatment with non-radioactive carbon monoxide. These explanations would not, however, suffice to explain the C^{14} distribution with time obtained on reducing the carbide in run 11c. This last experiment might mean that the carbiding of a sample of iron proceeds through the formation of a number of Fe_2C nuclei with additional reaction at the Fe_2C–Fe interface. Possibly C^{14} can diffuse rapidly through the iron phase during carbiding to deposit itself on the surface of the Fe_2C crystals deep within the iron matrix. On reduction, carbon can be removed from this Fe_2C–Fe interface (the carbon diffusing through the iron matrix to reach the surface) and also by direct attack on Fe_2C crystals at the gas–solid interface. Such a mechanism may possibly be made to account both for the time stability shown in Table II and for the reduction results of Fig. 3. However, clearly much more work is necessary before the mechanism of carbide formation can be said to be understood.

Exchange Experiments.—In order to interpret the synthesis runs correctly it was necessary to prove that the carbon in the reacting carbon monoxide and the hydrocarbon products was not exchanging rapidly with the carbide surface; a rapid exchange of this kind could give a false impression as to the part played by carbide in the synthesis.

These exchange experiments were performed by carbiding the reduced catalyst to about 60% Fe_2C with normal carbon monoxide and then a small additional amount with radioactive carbon monoxide. The surface activity was measured by partial reduction with hydrogen and then the hydrocarbon whose exchange was to be measured was admitted at the desired pressure and temperature. After a length of time, the gas phase was analyzed and its C^{14} activity found. The fraction exchange was calculated by dividing this activity by the activity the gas phase would have if the C^{14} in the surface layer of the catalyst were distributed uniformly in both the surface and gas phase.

$$\% \text{ exchange} = \frac{(N_0 + Y)C_g}{N_0 C_s^0} \times 100 \qquad (3)$$

when Y is the total cc. of carbon in the gas phase and the other terms have the same meaning as in equations 1 and 2.

The results of the exchange runs are given in Table IV. As can be seen from columns 7 and 10, butane, butene-1 and acetylene cracked when placed in contact with the catalyst but did not exchange.[8] The rate of cracking is increased very much if, before admitting the hydrocarbon, the catalyst surface is slightly reduced by hydrogen with liquid nitrogen around Trap F, Fig. 2.

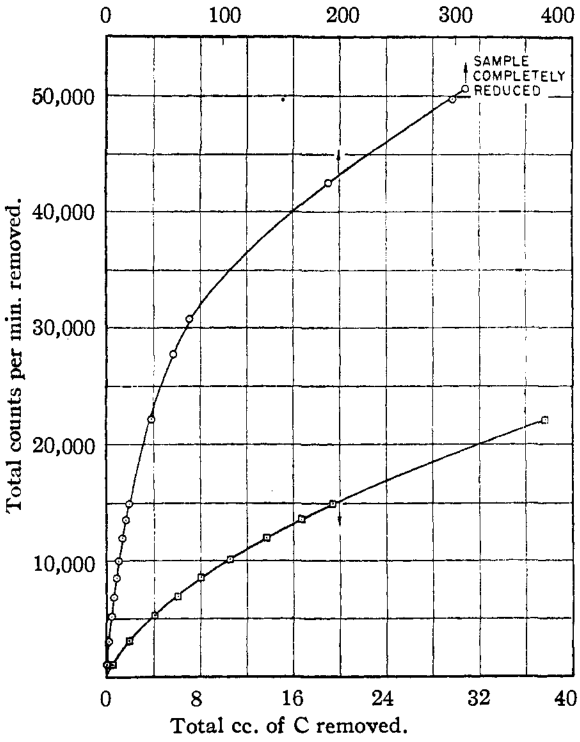

Fig. 3.

The carbon monoxide exchange at 250° is small as shown by run 7 but is appreciable at 322° as in run 8e. (It must be realized that considerable carbiding took place during this run.) In the actual synthesis runs the exchange between the carbon monoxide and the surface carbon was often determined and shown to be low (see column 7, Table VI).

To ascertain whether exchange might take place between methane and the products of synthesis, the following experiment was made. Catalyst B which had been carbided to 64.6% Fe_2C with normal carbon monoxide was used as a catalyst for the Fischer–Tropsch synthesis from 172 cc. of a 1:1, circulating, hydrogen:carbon monoxide mixture to which 39.3 cc. of radioactive methane of an activity of 5250 c./min./cc. had been added. Synthesis temperature was 253° and the duration was one-hundred fifty minutes. The results were:

	CO_2 produced by combustion, cc.	Activity, c./min./cc.
Gasol fraction	8.34	0 ± 1
Liquid hydrocarbons	3.58	0 ± 1

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[8] Even if the average surface activity or the final surface activity (column 9, Table IV) were used in place of C_s^0 in equation 3, the per cent. exchange of the hydrocarbons with surface C^{14} would still turn out to be ≦ ~ 4%.

TABLE IV

EXCHANGE DATA FOR 2.29 G. OF CATALYST B[a]

No.	Starting gas phase	Temp. of run, °C.	Time of run, min.	Pressure of run, mm.	Vol. of gas at beginning of the exp., cc. S. T. P.	Moles of C in gas phase per mole of gas phase after run	Surface activity c./min./cc. of C Before run	Surface activity c./min./cc. of C After run	Final gas phase activity, c./min./cc. of C	Gas phase activity for comp. exchange c./min./cc. of C	% exchange, eqn. 3
1e	Methane	253	960	60	5.01	0.98	610		0 ± 2	193	0 ± 1
2e	*n*-Butane	250	26	40	3.09	3.66	524		0 ± 2	83	0 ± 2.5
3e	*n*-Butane	250	127	40		2.16	524		0 ± 9	83	0 ± 11
4e	1-Butene	250	180	37	2.60	2.31	1127		4 ± 2	205	2 ± 1
5e	1-Butene	250	480	37		2.21	1127	610	4 ± 2	205	2 ± 1
6e	Acetylene	250	33	113–149	10.5	..[b]	610		0 ± 2 C_2H_2 only	61	0 ± 3
7e	Carbon monoxide	250	30	160–190	19.1	1.0	388	183	2 ± 1	41.7	5 ± 2
8e[c]	Carbon monoxide	322	7	140	10	1.0	1618		7 ± 1	24.3	29 ± 4

[a] The catalyst was carbided with CO to a Fe_2C content of about 60% before the runs. The surface of the sample before carbiding chemisorbed 4.64 cc. of carbon monoxide at −78° and therefore was assumed to have a "surface carbide" equivalent to 2.32 cc. of methane. [b] After the acetylene run, the gas phase analyzed: C_2H_2, 1.17 cc. with activity 0 ± 2 c./min./cc.; CH_4, 0.24 cc. with 369 c./min./cc.; H_2, 1.31 cc.; H_2O, 0.56 cc. [c] Catalyst A used for Run 8.

The experiment shows that methane in the gas phase does not exchange with the hydrocarbons during synthesis. This is important since methane of high activity is inadvertently produced during synthesis by partial reduction of the radioactive surface and is always present in the circulating system during synthesis.

The conclusion to be drawn from these exchange experiments is that we should expect very little exchange between the products of the Fischer–Tropsch synthesis and the surface carbide, once these products have reached the gas phase. Therefore, if the hydrocarbons produced during synthesis contain carbon atoms that were originally on the surface, it will reflect either exchange during the formation of the hydrocarbons or the participation of the iron carbide as an intermediate in the synthesis.

TABLE V

FISCHER–TROPSCH RUN (RUN 10S) ON CATALYST B CARBIDED TO 94.7% Fe_2C

Weight of reduced sample, 1.95 g.; temperature of run, 252°; time of run, 332 min.; pressure of run, 765–580 mm.; surface activity before the run, 1410 c./min./cc.; surface activity after the run, 745 c./min./cc.; synthesis gas contained 82.2 cc. H_2 and 80.1 cc. CO.

Produced or left, cc.		Activity	Unaccounted for, cc.	
CO	45.5	4.7 c./min./cc.	C	16.1
H_2	22.2		H_2	16.7
CH_4	5.1	199 c./min./cc.	O_2	2.75
CO_2	3.02			
$C_{2.6}H_5$	3.98	45 c./min./cc. of CO_2		
H_2O	23.1			

$$\left.\begin{array}{l}\text{Per cent. of total product formed}\\ \text{through } Fe_2C \text{ as an intermediate}\end{array}\right\} \frac{(45)\ (2)\ (100)}{1410 + 745} = 4.2\%$$

Synthesis Experiments.—The synthesis experiments were performed by circulating a hydrogen–carbon monoxide gas mixture over partially or fully carbided metallic catalysts in the apparatus and by the procedure described above. Table V gives the results of a typical run. Tables VI and VII summarize all the experimental results that were obtained in the course of the present work.

In all of the experiments it will be noted that the radioactivity of the methane and the other hydrocarbons formed during synthesis are always very much less than the average activity of the carbon present on the surface of the catalyst for those experiments in which the synthesis gas contained normal carbon monoxide and the surface contained the radioactive carbon. Also for the few experiments (runs 11S, 12S, 13S and 19S) in which the surface was carbided with normal carbon and the carbon monoxide of the synthesis gas contained C^{14}, the hydrocarbons synthesized were only slightly less radioactive per unit carbon than was the synthesis gas.

Obviously, if none of the hydrocarbon formation were occurring through the reduction of the surface carbide as an intermediate, the activity of the carbon in the hydrocarbon should be substantially the same as that of the carbon in the carbon monoxide in the synthesis gas. On the other hand, if all of the synthesis were occurring through the reduction of the surface carbide, then the carbon in the hydrocarbon should have the same activity as the average activity of the carbon in the surface (average of the surface activity before the run and the surface activity after the run). These statements can be expressed quantitatively by the equation

Per cent. of reaction through the carbide[9] =

$$100(C_s - C_p)/(C_s - \bar{C}_s) \quad (4)$$

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[9] Throughout the present paper it is assumed that the transfer of any of the carbon originally present on the catalyst surface to the gaseous hydrocarbon is an indication that the hydrocarbon has been formed by the reduction of the surface carbide. This seems especially warranted in view of the exchange experiments cited above which show that practically none of the radioactive carbon from the surface is transferred at synthesis temperatures to typical gaseous hydrocarbons circulated over the catalyst sample. However, it must

TABLE VI

SUMMARY OF DATA FOR SYNTHESIS RUNS

Synthesis Run no.	Catalyst	CO chemisorbed[a] at −78° on reduced catalyst sample, cc.	Activity[b] Surface before run	Activity[b] Surface after run	Activity[b] CO before run	Activity[b] CO after run	Produced in cc. gas S. T. P. H_2O	CO_2	CH_4 cc.	CH_4 Activity[b]	Gasol cc.	Gasol cc. of CO_2 from combustion	Gasol Activity[b]	Liquid cc. as CO_2	Liquid Activity[b]	H_2:CO ratio	Synthesis pressure, mm.
3S	B	4.0	910	282	0	11.2	39.3	49.8	8.3	49	10.9	23	45			1:1	730–320
4S	B	4.0	282	177	0	4	17.8	19.3	4.4	53	4.1	8.7	17			1:1	740–180
5S	B	4.0	1375	755	0		3.9	2.4			0.47	1.12	259			1:1	720–610
6S	B	4.0	594	565	0	2	4.9	2.6	0.6	100	.47	1.13	119			1:1	660–570
7S	B	4.0	634	523	0		3.0	2.0			.13	0.30	119			1:1	220–124
8S	B	4.0	362	368	0		8.0	2.2	1.66	39	.99	2.5	53			3:1	760–460
9S	B	4.0	1088	535	0	13	37.7	14.3	8.7	185	5.3	13.4	81			1:1	760–500
10S	B	4.0	1410	745	0	4.7	23.1	3.0	5.1	199	4.0	10.3	45			1:1	760–580
11S	B	4.0	0	(300)[c]	1768		4.9	0.2			0.14	0.38	1605			2:1	760–550
12S	B	4.0	0	(300)[c]	1768		4.3	0.8			.54	1.50	1580			2:1	550–320
13S	B	4.0	0	(300)[c]	1768		3.1	1.4			.59	1.20	1641			2:1	320–151
14S	B	4.0	(300)[c]	218	0		4.0	0.6			.46	1.18	33			1:1	760–662
15S	C	4.4	659	334	0	<8	7.6	0.8	>0.6	157	.84	2.34	66	1.52	110	2:1	800–680
16S	C	4.4	334	193	0						2.9	7.02	26	3.6	45	2:1	700–200
19S	D	(13.2)[e]	0	754	1520	1491	2.0	24	3.9	1085	3.6	3.67	1289	4.7	1069	1:1	760
22S	B	5.4	1700[d]	450	0		7.7	20			3.2	8.9	80.6	3.9	80.8	1:1	760–156
23S	B	5.4	450	339	0		10	17.4			3.5	10.4	30.1	3.7	30.5	1:1	760–234
24S	B	5.4	1810[d]	1530	0		0.87	0.27			0.09	0.23	314	0.03	506	1:1	730–690
25S	B	5.4	1530	1290	0		1.49	0.40			.15	.40	169	0.09	182	1:1	620–580
26S	B	5.4	4780	793	0		9.8	5.9			.41	.92	361	0.77	192	1:1	800–500
27Sa	B	37.2	5950		0			.20				.12	561			1:1	760
27Sb	B	37.2	[f]		0			.28				.16	625			1:1	760
27Sc	B	37.2	[f]		0			.70				.38	578			1:1	760
27Sd	B	37.2	[f]	5180	0			1.33				.74	500			1:1	760
28S	B	37.2	5180		0							.25[g]	494			1:1	760
29S	B	37.2	8680		0							.76[g]	932			1:1	760
30S	B	37.2	[f]		0							.39[g]	1430			1:1	760
31S	B	37.2	[f]		0							.23[g]	1150			1:1	760

[a] Catalyst wt. = 2–3 g. except for runs 27S to 31S for which it was 30 g. [b] Activity given in counts per minute per cc. of carbon dioxide after combustion. [c] Estimated. [d] Calculated from previous data. No surface hydrogenation. [e] This is the volume of physically adsorbed nitrogen in a monolayer; no carbon monoxide chemsorption was made on this sample. [f] In runs 27Sa, 27Sb, 27Sc, and 27Sd, a surface activity was measured only at the beginning and the end of the series; in run 28S and 29S, no final surface activity was measured; in runs 30S, and 31S, the surface activity was assumed to be the same as in run 29S. This seems like a reasonable assumption since these were all very short runs with little opportunity for the surface activity to be altered. [g] The gasol and liquid fractions were combined in runs 28S, 29S, 30S and 31S.

where C_g is the original activity of the carbon monoxide used in the synthesis gas; C_p is the activity of the carbon in the hydrocarbons synthesized, and $\overline{C}_s$ is the average of the activity of the surface carbon taken immediately before and immediately after the synthesis runs. All of these activities are expressed in the tables as actual counts per minute per cc. of carbon dioxide formed by the combustion of the carbon monoxide or of the hydrocarbons being analyzed.

The application of equation 4 is well illustrated in Table V by the data and the calculation of a typical run. It will be noticed that whereas the carbon in the surface of the catalyst had an average activity of (1410 + 745)/2 or 1078 counts per minute per cc. of carbon, the carbon on the synthesized hydrocarbon (other than methane) had an activity of only 45 counts per minute per cc. of carbon dioxide formed by burning the hydrocarbon. In other words only about 4% of the reaction appears to have proceeded by the reduction of surface carbide as an intermediate.

Two other things should be noted in Table V: (1) the carbon monoxide at the end of the run had a negligibly small radioactivity. This conforms to the prediction one would have made from experiment 7e (Table IV). (2) A certain fraction of the carbon, oxygen and hydrogen of the original gas is always unaccounted for when one makes a mass balance of a run. This unaccounted-for material presumably is left on the surface after evacuation at the end of the run as carbide, oxide, and higher hydrocarbon. This unaccounted-for portion of the reactants usually amounts to about 20% of the original synthesis gas and is considered not to affect the conclusions drawn from the present work.

The data for the runs on catalysts B, D and C are shown in Table VI. Calculations for the fraction of the reaction going by way of iron carbide

be remembered that the possibility has not been excluded that methylene groups adsorbed on the surface during synthesis might be able to exchange carbon atoms rapidly with the surface. If this were the case, then the part of the reaction assumed to take place by carbide reduction might actually be occurring by some process not involving the reduction of the surface or bulk carbide. Accordingly, equation 4 yields maximum values for the per cent. of the reaction that can be taking place by the reduction of carbide, provided, of course, the surface is behaving uniformly. The question of the extent to which active points can be involved will be discussed presently.

TABLE VII

APPARENT PER CENT. OF THE HYDROCARBON SYNTHESIS PROCEEDING BY WAY OF CARBIDE REDUCTION

Synthesis Run	Catalyst	Fe_2C, %	Synthesis temp., °C.	Per cent. of product formed through carbide		Fraction of the carbon (Fe_2C) surface of the catalyst which the product represents[b]	Synthesis rate cc. of C synthesized per min. per g. of metal in reduced sample[a, b]	Comments
				Gasol	Liq.			
3S	B	~61	300	9		11.5	0.24	
4S	B	~73	300	7.5		4.3	.06	This run immediately following run 3S
5S	B	~80	300	24		0.56	.06	
6S	B	~81	300	16		.56	.06	
7S	B	~81	300	20		.15	.016	
8S	B	~82	300	14		1.25	.13	
9S	B	~87	300	10		6.7	.07	
10S	B	~94	252	4.4		5.2	.024	
11S[f]	B	75.7	260	11		0.19	.019	
12S[f]	B	75.7	260	13		.75	.019	
13S[f]	B	75.7	260	8.7		.60	.009	Normal CO used in synthesis gas immediately following run 13S
14S	B	76	260	12.7		.59	.024	
15S	C	70	200	13	22	1.75	.034	
16S	C	~71	200	10	17	4.8	.015	
19S[f]	D		240	19	38		.054	
22S	B	67	244	7.5	7.5	4.8	.58	
23S	B	70	244	7.7	7.7	5.2	.63	
24S	B	*ca.* 110[e]	244	18	30	0.10	.012	
25S	B	*ca.* 110[e]	244	12	13	.18	.013	
26S	B	4	203	13	7	.63	.141	Carbided only with radioactive CO
27Sa	B	80	240	10.1		.0062	.0077	Flow system[d]; large sample of catalyst; 1 atmosphere pressure. 27a, 27b, 27c, and 27d represent 4 successive samples taken in the same synthesis run. Product in column 7 as fraction of surface is cumulative in these 4 samples. In runs 28S, 29S, 30S, and 31S mercury cutoffs were used in place of stopcocks at the exit of the reactor.
27Sb	B	80	240	11.2		.015	.0053	
27Sc	B	80	240	10.4		.035	.0063	
27Sd	B	80	240	9.0		.075	.0063	
28S	B	80	240	9.5[c]		0.014	~0.005 to 0.01	
29S	B	85	303	10.7[c]		.041	~ .005 to .01	
30S	B	85	303	16.5[c]		.021	~ .005 to .01	
31S	B	85	303	13.3[c]		.012	~ .005 to .01	

[a] Typical synthesis rate for commercial catalyst at one atmosphere (60 g. of hydrocarbon per m^3 and at a flow of 4 liters per hour per 10 g. of catalyst) is 0.64 cc. of C per min. per g. of catalyst. [b] Includes only gasol fraction in runs 3S to 14S and in run 27S. [c] In runs 28S, 29S, 30S and 31S the gasol and liquid fractions were combined before analysis. [d] Circulating system was used in all runs except 27S to 31S, inclusive. [e] More carbon was picked up by this sample than corresponded to complete conversion of the Fe to Fe_2C. Presumably, some free carbon was formed. [f] For these runs $C^{14}O$ was present in the synthesis; the surface contained normal C. In all other runs, the surface contained C^{14} and the synthesis gas contained non-radioactive CO.

as an intermediate are shown in columns 5 and 6 of Table VII and are plotted in Fig. 4 as a function of the ratio between the amount of carbon in the synthesized hydrocarbons and the amount that would be required to form a monolayer on the iron surface of the catalyst (assuming the surface carbon to be present in a ratio of one carbon atom for each two surface iron atoms). As can be seen from Fig. 4, the data clearly indicate that at temperatures of about 260° or less, an average of about 10% of the synthesized hydrocarbon appears to have been formed by carbide reduction, regardless of the pressure of synthesis gas, the per cent. Fe_2C present or the ratio of hydrogen to carbon monoxide in the synthesis gas. The one exception, run 24S, showed 18% going by the carbide. However, this was a very slow, long run on an extremely heavily carbided sample with the smallest total product formation (0.09 cc. of hydrocarbon gas) of the entire series of runs. Furthermore, a duplicate run, 25S, with about twice the product yield, showed only 12% going by way of carbide. Hence, run 24S can probably be disregarded as containing a large experimental error.

The twor uns (15S and 16S) made on a standard reduced cobalt catalyst give a result similar to that obtained on iron catalysts and indicate that the carbide reduction mechanism on cobalt plays a minor role also in the synthesis that occurs over that metal. This result is in accord with recent publication by research workers at the Bureau of Mines at Pittsburgh.[10] They have obtained evi-

(10) S. Weller, THIS JOURNAL, **69**, 2432 (1947).

dence not only that bulk cobalt carbide is not an intermediate in Fischer–Tropsch synthesis but also that it is not even a catalyst,[11] since the rate of synthesis on a heavily carbided cobalt catalyst is much less than on one containing little or no carbide.

One run was made on catalyst D. The sample, after being dried at 300°, was pretreated with carbon monoxide for twenty-four hours at 325° and at 0.1 atmosphere pressure. It was then used at 240° for six and one-half hours as a catalyst in a flow system with a 1:1 hydrogen:carbon monoxide mixture passing over the catalyst at a space velocity of about 800. At the end of this time the catalyst was evacuated at 240° and used as a catalyst in run 19S in a circulating system such as was employed in the other runs. This single run gave a high value, 19%, for the per cent. of the reaction that appeared to go by way of carbide reduction. This run should, however, be given less weight than the others because of the fact that it was run with a mixture of hydrogen and radioactive carbon monoxide immediately after the 6.5-hour synthesis run in a flow system with a synthesis gas containing normal carbon monoxide. It seems quite probable that some of the normal carbon getting into the product from the radioactive run was from non-radioactive hydrocarbons still adsorbed on the catalyst at the start of the run.

It was of interest to ascertain whether or not the apparent per cent. of the reaction going by way of carbide reduction was a function of the molecular weight of the product since it seemed reasonable that the higher molecular weight material might, in its longer residence on the catalyst, have been more likely to have undergone some exchange with the radioactive carbon in the surface than would the gasol fraction. Accordingly, in a few runs, the analysis was carried out separately for the portion of the hydrocarbon product that vaporized from the trap at room temperature but did not vaporize at −78°. Runs 22S to 26S, inclusive, showed no higher percentage of the reaction going by the carbide reduction for the higher molecular weight material than for the lower molecular weight product, with the exception of experiment 24S which, for reasons discussed above, is of doubtful validity. Run 19S on the iron oxide catalyst also showed a higher percentage by carbide reduction but, as mentioned above, should not be given too much consideration because of adsorbed hydrocarbons, containing normal carbon, having probably been present at the start of the run with radioactive synthesis gas. Only the two cobalt runs (15S and 26S, Table VII) gave a consistent indication that the higher molecular weight product might have been produced to a greater extent by carbide reduction than the lower molecular weight material, or might have undergone more exchange with the radioactive surface carbon during synthesis.

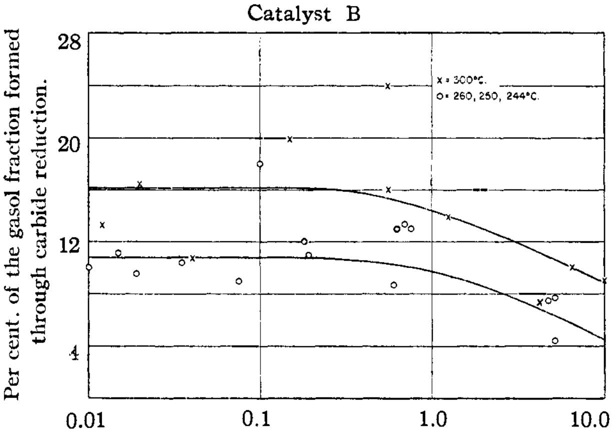

Fig. 4.

Less importance and significance was attached in the present work to the radioactive content of the methane formed than to that of the higher hydrocarbons because it was understood from preliminary work that the gradual reduction of the radioactive surface by the hydrogen present during the synthesis run could proceed to form methane concomitantly with the synthesis of this product by some adsorptive or other process not involving the reduction of carbide. Nevertheless, it is interesting to note that, as can be calculated from the data in Table VI, the apparent per cent. of the methane formation going by way of carbide reduction varied from 8 to 23% for catalyst B, was 32% for the cobalt catalyst in run 15S and was 37% for the iron oxide catalyst in run 19S. These results agree with the expectation that for a radioactive surface and normal synthesis mixture, the radioactivity of the carbon in the methane would on an average be a little higher than that of the other hydrocarbons; they also show, however, that even this hydrocarbon is formed predominantly by some process other than the reduction of the carbide that is present.

In summarizing the above discussion it seems fair to conclude that, for the most part, the mechanism of hydrocarbon production by carbide reduction proposed by Fischer and his co-workers plays only a minor role in the synthesis of hydrocarbons under the conditions and over the catalyst studied in the present work, provided one assumes that the surface is uniformly active in the synthesis.

In recent years it has been suggested[12] and demonstrated[13] that the surfaces of various catalysts, including iron synthetic ammonia catalysts[14] appear to be heterogeneous and that catalytic reactions may occur predominantly on a small fraction of the surface that has been designated as containing the "active points." The question

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[11] Weller, Hofer and Anderson, *ibid.*, **70**, 799 (1948).

[12] Taylor, *Proc. Roy. Soc.* (*London*), **A108**, 105 (1925); *J. Phys. Chem.*, **30**, 145 (1926).

[13] Pease and Stewart, THIS JOURNAL, **47**, 1235 (1925).

[14] Brunauer, Love and Keenan, *ibid.*, **64**, 251 (1942).

now arises as to whether or not the data in Table VI afford any evidence as to the possibility of such active points participating in the present synthesis experiments and as to the influence that such surface heterogeneity would have on the conclusions as to the fraction of the synthesis occurring by way of carbide reduction.

A little reflection will show that if most of the hydrocarbon synthesis were occurring through active points then most, or all, of the synthesis might actually be occurring through a mechanism of carbide reduction. For example, suppose 3 or 4% of the surface were synthesizing 90% of the hydrocarbon and that the other 10% of the hydrocarbons were being synthesized by the rest of the catalyst. Clearly the 3 or 4% of the surface would soon reach an isotopic composition similar to that of the carbon in the gas phase. In other words, the active points would soon be so thoroughly "washed" by the gas phase that their radioactivity per unit carbon content would no longer differ from that of the gas phase. Yet, an assay of the surface activity at the end of the run would show the surface as a whole to be highly radioactive, provided the reduction of the surface carbide by hydrogen proceeds uniformly over the active patches and the rest of the surface. One might then erroneously conclude that 90% of the reaction was occurring by other than a carbide reduction mechanism.

To eliminate the possibility of active points being a major disturbing factor, two types of experiments were performed. In one group of runs (experiments 27Sa, 27Sb, 27Sc, 27Sd, 28S, 29S, 30S and 31S) care was taken to synthesize an amount of hydrocarbon corresponding to only a very small fraction of the surface. If active points covering several per cent. of the surface were involved, one would expect that when the total amount of hydrocarbon synthesized was made to correspond to a smaller and smaller fraction of the surface carbon, the apparent per cent. of the reaction going by way of the carbide mechanism would rise. In contrast to this, experiment 27Sa shows that even when the hydrocarbon synthesized contains carbon equivalent to only 0.62% of a monolayer, the apparent per cent. of the reaction going by way of carbide as calculated by equation 4 is 10% at a temperature of 240°. This means that if active points are responsible for most of the synthesis, they must constitute much less than 0.5% of the surface of the catalyst.

A second type of evidence that argues against the possibility of active points causing most of the synthesis is the fact that successive experiments (runs 27a, 27b, 27c and 27d) taken without intervening evacuation show that the apparent per cent. of the reaction going by way of the carbide is constant. If active points were influencing the results one would have expected successive runs, or successive samples in a single run, to give successively smaller apparent percentages of the reaction proceeding by way of the carbide mechanism as calculated by equation 4.

At the conclusion of run 27S it was realized that one source of possible error had not been eliminated. The samples of hydrocarbon obtained in this run had been collected by a cold trap after having passed through a greased stopcock. The possibility, therefore, suggested itself that the product might have been contaminated by small amounts of hydrocarbons containing normal carbon that may have vaporized from the stopcock grease, or that the first part of the hydrocarbon formed might have dissolved in the stopcock grease. To eliminate this possibility, the stopcock was replaced by a mercury cutoff and the run repeated. Run 28S taken at 240° shows that apparently the results of run 27S were real and were not influenced by the greased stopcock.

With this mercury cutoff in the line runs 29S, 30S, and 31S were made at about 300°, to ascertain whether or not the apparent per cent. of the reaction going by way of the carbide even at this higher temperature would rise rapidly if one took hydrocarbon samples corresponding to smaller and smaller fractions of a monolayer of carbide carbon on the surface of the catalyst. The results like those at 240° show that the per cent. of the reaction going by way of the carbide shows no rise at hydrocarbon yields equivalent to the carbon in only a few per cent. of the surface.

Experiments 27S to 31S, inclusive, taken as a whole, seem to show conclusively that if a carbide reduction mechanism is predominant in forming CH_2 groups for hydrocarbon synthesis, then the part of the surface covered by such active points must be very small—probably smaller than 0.05% of the total surface. Of course, none of the experiments here performed preclude the possibility of most of the reaction going by way of even large active patches provided the mechanism involved on these active points is something other than carbide reduction and formation.

One other possible type of irregularity had to be taken into consideration. If, during the carbiding with normal carbon monoxide, the active points, planes or particles of the catalyst were so completely carbided that the later treatment with radioactive carbon monoxide placed C^{14} atoms on only the less active part of the surface, then the synthesis experiment using normal carbon monoxide would be deceptive, for all of the reaction might be occurring by a carbide mechanism on the active part of the surface which, according to the assumed characteristics of the carbiding, would from the start contain only normal carbon atoms. To obviate the possibility that such a surface non-uniformity was introducing an error in our work, a number of runs were made in which the surface was carbided only with normal carbon monoxide, and the synthesis gas contained the radioactive carbon monoxide. Runs 11S, 12S and 13S were of this type. The fact that the apparent per cent. of the reaction going by way of carbide was the same for these runs as for those done at similar temperatures but with normal carbon monoxide in the synthesis gas and a radioactive surface shows that this type of irregularity was not influencing our results.

If the experiments reported in the present paper are considered in great detail, some ambiguity may arise as to what is meant by the term "carbide" when we conclude that only a small fraction of the reduction appears to proceed by way of the reduction of "bulk or surface carbide." It must be apparent from the method of procedure described above that this expression refers to any form of carbide left on the catalyst by the precarbiding process employing pure carbon monoxide. Accordingly, any form of bulk carbide or surface carbide that is left on the catalyst surface at the start of the synthesis run is included in the general term "carbide" as used throughout the present work. On the other hand, it should be made clear that nothing in the present work precludes the possibility that carbon atoms formed on the surface during synthesis (as for example, by the reaction of hydrogen and carbon monoxide to form water and a surface carbon atom) may be bound to the metallic phase by the same type chemical bond involved in the formation of metal carbides and may react with hydrogen to form CH_2 groups which then polymerize to stable hydrocarbons. Whether one should call a carbon atom left on a metallic phase momentarily as a result of some reaction of the synthesis gas "adsorbed carbon" or "surface carbide" carbon is, after all, very much a matter of nomenclature. Some may wish to call such a formation of carbon atoms on a metallic surface from synthesis gas an "incipient carbide" formation. With this terminology, there can be no quarrel since it seems very likely that such carbon atoms would be held to the metallic surface by the same type of chemical bonds involved in carbide formation. Accordingly, it should again be emphasized that the present results merely show that the kind of bulk or surface carbide left by precarbiding with carbon monoxide does not play an important part in the synthesis of hydrocarbons over Fischer–Tropsch cobalt or iron catalysts. It is still possible that an "incipient surface carbide" formed on the surface during synthesis may be an intermediate in hydrocarbon formation over these catalysts.

In the present work we have referred continually to hydrocarbon formation. Actually, in some runs the oxygen balance on combustion analysis indicated that a small per cent. of the products of synthesis was oxygenated compounds. This is not surprising since it is well known[12,13] that runs over iron catalyst at somewhat higher pressure than those here employed usually result in the formation of considerable amounts of alcohols.

Finally, it should be noted that the results here reported are for metal catalysts operating under the conditions here described at pressures given in Table VI and usually the order of one atmosphere. All of the catalysts yielded hydrocarbons in amounts that are smaller than those produced during commercial synthesis (see Table VII, column 8). The rates of synthesis seemed especially low when more than 70% of the iron catalyst was initially converted to Fe_2C. Accordingly, strictly speaking, the mechanism results here reported must be restricted to the smaller amounts, of hydrocarbons here synthesized, although actually, there seems little reason to believe that the higher yield of hydrocarbon obtained in commercial synthesis should show any higher fraction going through a carbide reduction mechanism than observed in the present work.

Summary

Fischer–Tropsch synthesis experiments using C^{14} as a "tracer" show that the greater part of the product of synthesis is formed by some process other than by the reduction of carbide as an intermediate. Only about 10% of the hydrocarbon product appears to have been formed through the carbide for iron catalysts at or below 260° and for cobalt at 200°; at 300° the part of the reaction occurring through the carbide reduction mechanism seems to average about 16%. The per cent. formed through the adsorbed phase is not critically dependent on the hydrogen:carbon monoxide ratio in the range 1:1 to 3:1, on the total pressure of the synthesis, within the limits 150 to 800 mm. pressure; or on the per cent. Fe_2C initially present in the range 4 to 100%.

The exchange of the carbon in the gases, methane, butane, butene-1, and acetylene, with an iron carbide surface at 250° is found to be very low; carbon monoxide exchange with the carbon in the carbide is only about 5% in thirty minutes at 250° but is as high as 29% in seven minutes at 322.

The mechanism of carbiding has been investigated and has been shown to be complicated by the possibility of a non-uniformly reacting surface. No completely satisfactory picture of the mechanism of carbiding has been formulated.

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[12] Holroyd, Combined Intelligence Objectives Committee. Report 30, 32/107, 1945.

[13] Keith, *Oil Gas J.*, **45**, No. 6, 102 (1946).