The preparation of isopropylacetylbenzoylmethane is reported for the first time.

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[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES]

THE MECHANISM OF THE FORMATION OF HIGHER HYDROCARBONS FROM WATER GAS[1]

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Introduction

In April, 1926, Fischer and Tropsch[5] announced that higher homologs of methane are formed when mixtures of hydrogen and carbon monoxide are passed at atmospheric pressure over catalysts of iron or cobalt mixed with various supporting materials, at temperatures from 250 to 300°. The catalysts were stated to have been prepared by reduction from the oxides with hydrogen at 350°. It was said that no oxygen-containing organic compounds were found. The mechanism of the process was thought to be through formation of metallic carbides, although it was found impossible to obtain the higher paraffins by passing hydrogen alone over the supposed carbides. Upon further examination, Fischer and Tropsch[6] announced the product to consist of ethane, propane, butane and higher homologs up to solid paraffin, with only inappreciable amounts of olefins. It was said that a wide range of space velocities and CO–H_2 mixtures were used. Elvins and Nash[7] reported the formation of oily material on a cobalt–manganese oxide–copper catalyst at atmospheric pressure and temperatures from 245 to 284°. The yields were small, however. In July, 1926, Elvins and Nash[8] reported the presence of oxygen-containing compounds in addition to hydrocarbons in this product. Fischer and Tropsch[9] stated that oxygen-containing compounds were present in their product in only very small quantities compared to the amounts of hydrocarbons produced. At the September, 1927, Meeting of the American Chemical Society, Smith, Davis and Reynolds gave results of preliminary work in which olefin as well as paraffin hydrocarbons were obtained. Full details of this work

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[5] Fischer and Tropsch, *Brennstoff-Chemie*, **7**, 97 (1926); *Ber.*, **59**, 830, 832 (1926).

[6] Fischer and Tropsch, *ibid.*, p. 923.

[7] Elvins and Nash, *Fuel*, **5**, 263 (1926).

[8] Elvins and Nash, *Nature*, **118**, 154 (1926).

[9] Fischer and Tropsch, *Brennstoff-Chemie*, **7**, 299 (1926).

were published later.[10] In December, 1927, Elvins[11] published the results of further work. The catalyst preparation received further attention and the products were examined more closely. Olefin and paraffin hydrocarbons were found as well as oxygen-containing compounds. Temperatures of 280–320° were used. In January, 1928, Fischer and Tropsch[12] gave the results of extensive examination of the gaseous and liquid hydrocarbons obtained. They report the presence of oxygen-containing compounds in small amounts and of only olefin and paraffin hydrocarbons. They stated that their products were obtained at reaction temperatures of around 190° on a cobalt–copper catalyst. Several hydrocarbons were identified. The presence of acetone and aldehydes in the water layer was claimed. Later, Smith, Hawk and Reynolds[13] presented complete results of the formation of olefin and paraffin hydrocarbons on a cobalt–manganese oxide–copper catalyst at temperatures of 200–260°. Good conversions were obtained, the lower hydrocarbons were completely analyzed, and complete information on the procedure was presented. The catalyst used here was much more active than the one used by Elvins and Nash. Since Fischer and Tropsch have not presented complete details of their work, it is not known just how active their catalysts were. Further examination of the hydrocarbon product by Tropsch and Koch[14] resulted in identification of various olefin and paraffin hydrocarbons. It showed the absence of naphthenes, but small quantities of benzene and toluene were found.

Nature of the Reactions

Elvins and Nash[8] suggest that the formation of oxygen-containing compounds is an intermediate step in the formation of hydrocarbons. Elvins[11] suggests that carbonyls are intermediate products. The latest presentation of the ideas of Fischer and Tropsch[12] on the possible mechanism of the process is outlined under (1), (2), (3) and (4) as follows. (1) Methylene (CH_2) may be formed primarily from hydrogen and carbide carbon, which is in turn at once polymerized to higher hydrocarbons. (2) Complex molecules of three and four carbon atoms may form as primary reaction products which also may in turn suffer polymerization. This possibility is discussed since propylene and butylene are the principal products when iron carbide is decomposed by acids, but the presence of ethylene and ethane in the synthetic product argues against this. (3) High molecular weight hydrocarbons may be formed in a primary act. These may undergo cracking on the catalyst. Thermodynamic relationships, Fischer and

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[10] Smith, Davis and Reynolds, *Ind. Eng. Chem.*, **20**, 462 (1928).

[11] Elvins, *J. Soc. Chem. Ind.*, **46**, 473T (1927).

[12] Fischer and Tropsch, *Brennstoff-Chemie*, **9**, 21 (1928).

[13] Smith, Hawk and Reynolds, *Ind. Eng. Chem.*, **20**, 1341 (1928).

[14] Tropsch and Koch, *Brennstoff-Chemie*, **10**, 337 (1929).

Tropsch think, argue for this. (4) Secondary hydrogenation of olefins always occurs.

Passage of hydrogen alone over the supposed carbides produces no higher hydrocarbons, so that the "carbide theory" receives no support from this source. However, if the "carbides" are supposed to exist only transitorily and in the relatively small amounts which would be necessary to explain the catalysis, this theory becomes difficult to prove or disprove. In regard to possibility (3) above, obviously the fact that thermodynamically the formation of the very high hydrocarbons from water gas is possible, can have no bearing on the question of the mechanism. Before thermodynamic information was available it had been shown possible to derive these products from water gas under the experimental conditions of the process.

Evidently a reaction such as

$$20CO + 40H_2 = C_{20}H_{40} + 20H_2O$$

which is known to represent an over-all experimental result, can scarcely be imagined to take place in one step and at a rapid rate. In this sense, the reaction is a quite remarkable one. In an attempt to explain the mechanism of the reactions and to find means of better controlling them, the experimental work to be described herein was undertaken.

Experimental Work Using Cobalt-Copper-Manganese Oxide Catalysts

The general nature of the apparatus and method has been described elsewhere.[13] The possibility that cracking of the heavier hydrocarbons might occur on the catalyst during the process of their synthesis was first investigated. Using the cobalt-copper-manganese oxide catalyst previously described, a sample of our synthetic hydrocarbon oil (from which the products below pentane and amylene had been removed) was flushed over the catalyst at 206° with 137 liters of pure nitrogen in three hours. The original oil had a density of 0.7031, an iodine number (Wijs) of 42.5 and weighed 20.83 g. The product collected after passage over the catalyst had a density of 0.7024, an iodine number of 42.0 and weighed 19.56 g. Only very small amounts of gaseous hydrocarbons were found in the nitrogen passing through. Thus no considerable amount of cracking (or polymerization) of these heavy hydrocarbons occurs and Fischer and Tropsch's suggestion, Number 3 above, seems to be excluded as far as forming any large part of the mechanism.

Next, it was desired to determine whether polymerization of the lower olefins occurred. Accordingly, pure ethylene was passed over the catalyst. No reaction whatever was observed. Similarly, a mixture of ethylene and hydrogen produced only ethane. Thus it seems that polymerization of ethylene is not a factor in the mechanism.

Mixtures of ethylene and carbon monoxide, when passed over the catalyst, gave no reaction. Likewise, ethylene and water vapor gave no reaction.

Since acetone was found by Fischer and Tropsch[12] to be a principal organic oxygen-containing compound, some experiments were undertaken to determine whether acetone might be an intermediate product in the formation of hydrocarbons. When a mixture of nitrogen and acetone vapor was passed over the catalyst at 206°, 4 to 7% of the acetone was converted to an oily product insoluble in water. Small amounts of hydrogen and methane appeared in the gas. The oil contained no acid or aldehyde. It was unsaturated. When a mixture of hydrogen and acetone was passed over the catalyst a considerable amount of hydrogen entered into reaction and considerably more methane was produced than was the case without hydrogen. A considerable amount of the product boiled in the range of ethyl alcohol, gave qualitative tests for primary and secondary alcohols, and contained no acid or aldehyde. About 0.1 cc. of heavy oil was produced. It melted from −2 to +15° and was unsaturated. Some ethane appeared in the gas. Then, 55 g. of acetone was passed over the catalyst at 206° with 77 liters of water gas during the course of one and one-half hours. About 12 g. of the acetone entered into reaction. The product, aside from the usual hydrocarbons obtained from water gas alone, gave qualitative tests for primary, secondary and tertiary alcohols. Apparently, hydrocarbons may be produced from acetone. The hydrocarbons so formed, however, are different in character from those obtained from water gas. Although it is possible that some hydrocarbons arise through intermediate formation of acetone, the latter is practically never found in appreciable amount in the products and the results about to be described furnish a much better picture of the mechanism.

Although ethylene did not produce higher hydrocarbons either alone or in the presence of hydrogen or carbon monoxide, it was thought that in the presence of both hydrogen and carbon monoxide, this reaction might take place. Table I shows the results of the first experiments with ethylene–water gas mixtures. In the table it is to be noted that all gas volumes are reduced to standard conditions of temperature and pressure. In the data in this and following tables on products formed, g./l. H_2, etc., means grams of product obtained per liter of H_2, etc., converted in the process. The experiments were carried out in the order in which they are recorded in the table and with the same sample of catalyst (cobalt–copper–manganese oxide). They were all run at the same temperature and approximate rate for purposes of comparison. The straight water-gas experiments (the first and last in the table) were made in order to determine whether the activity of the catalyst was changing. Evidently the activity had remained substantially constant. The catalyst was flushed out with pure hydrogen overnight between experiments in order to assure that it remained free of

Table I

Preliminary Experiments with C_2H_4–CO–H_2 Mixtures (250 Cc. of Catalyst)

Expt.	Temp., °C.	Flow rate liters/min.	Gas entering, liters				Gas leaving, liters			Gas converted, liters		
			H_2	CO	C_2H_4	N_2	H_2	CO	C_2H_4	H_2	CO	C_2H_4
1	204	1.18	126	111	0	0	99	93	0.3	27	17	0
2	204	1.15	78	67	81	0	14	52	29	64	15	52
3	204	1.21	79	66	0	84	64	55	0.2	16	11	0
4	204	1.15	122	104	0	0	98	91	0.2	25	13	0

Expt.	Products formed								
		Pentane and higher							
	C_2H_6 liters	g.	g./l. H_2	g./l. CO	g./l. H_2 + CO	CO_2 (g.)	H_2O (g.)	Sp. gr. of oil, 20°/20°	Iodine no. of oil
1	0.32	4.40	0.16	0.26	0.10	2.62	10.73	0.7120	73
2	40.5	12.69	.20	.86	.16	2.57	9.53	.7320	73
3	0.28	3.31	.21	.30	.12	1.98	7.87	.7219	79
4	..	4.38	.18	.34	.12	3.07	10.10	.7192	73

accumulated products and was completely reduced. Of course, oxidation of the catalyst by a trace of oxygen in the gas requires subsequent treatment with hydrogen at a higher temperature in order to reduce the catalyst completely. Analyses of the hydrocarbon products between ethane and pentane are not presented since they are not important for the present purposes. This fraction, however, was considerable in amount in an ethylene experiment as compared with that in a water-gas experiment. The yields are expressed in total liters or grams and in grams per liter of reactants converted in the process.

The original oil yield was separated from the water layer and carefully fractionated in a small apparatus to remove hydrocarbons lower than those of five carbon atoms.

In comparing Expts. 2 and 3, in which the partial pressures of carbon monoxide and hydrogen are the same but nitrogen has replaced ethylene, the striking thing is the large yield of oil in the presence of ethylene. Naturally, a large amount of ethylene is hydrogenated to ethane but about 11 liters of ethylene has been converted to oil. Due to the removal of hydrogen to form ethane, the yield of oil per liter of hydrogen converted is small, but the yield per liter of carbon monoxide converted is very large in Expt. 2. The larger consumption of carbon monoxide in Expt. 2 (reflected in the larger amounts of carbon monoxide and water appearing in the products) indicates that more of it enters into oil formation in the presence of ethylene. As was discovered later, the "oil" contains a considerable amount of oxygen-containing compounds. Recalling that ethylene does not react either alone or in the presence of either hydrogen or carbon monoxide, we find, however, when both carbon monoxide and hydrogen are present with ethylene, the latter enters into a reaction which produces heavier products. Thus, it seems that hydrogen and carbon monoxide react to produce substances on the catalyst surface with which ethylene is capable of reacting.

Upon examination of the product obtained from ethylene–water gas mixtures, it was found to contain 25 to 35% of water-soluble material (oxygen-containing compounds). This accounts for the higher density of the oil in Expt. 2. Of course, some of the water-soluble material was in solution with the water produced in the experiment, so that the total yield of organic products recorded in Expt. 2 should be increased by the amount which was removed with the water layer and the recorded amount of water should be decreased a corresponding amount. In an experiment at 210° in which the flow rate was 1.84 liters/minute and the ethylene concentration was 20 to 25%, the following results were obtained: original oil layer, 15.0 cc. (containing 30% of water-soluble material); original aqueous layer, 18.5 cc. Fractionation of this material gave: water, 14.0 cc.; hydrocarbon oil, 10.0 cc.; water-soluble organic material, 9.1 cc. Of course, due to possible existence of constant-boiling mixtures of water-soluble material with the water, the separation of the latter probably is not complete. In an ordinary experiment with water gas alone no appreciable amounts of water-soluble material were found in the oil, although a trace of aldehyde was usually present.

Comparison of Expts. 3 and 4 shows the effect of changing the partial pressures of carbon monoxide and hydrogen when the ratio CO:H_2 remains the same. At the lower partial pressures the amount of hydrogenation is less, as shown by the larger iodine number of the product in Expt. 3, and is reflected in the slightly increased yield of oil per liter of hydrogen converted. The presence of more unsaturated material in Expt. 3 is reflected in the higher density of the oil.

The results in Table II are presented in order to show the composition and amount of the intermediate hydrocarbon fraction in an ethylene experiment as compared with that in an experiment with water gas alone. Analysis of the intermediate hydrocarbon fraction was made using a modified Shepherd–Porter apparatus.[15]

TABLE II

COMPARATIVE EXPERIMENTS SHOWING COMPOSITION AND AMOUNT OF INTERMEDIATE HYDROCARBON FRACTION (250 CC. OF CATALYST)

Expt.	Temp., °C.	Flow rate, liters/min.	Gas entering (liters)			Gas leaving (liters)			Gas converted (liters)		
			H_2	CO	C_2H_4	H_2	CO	C_2H_4	H_2	CO	C_2H_4
1	245	1.22	87	75	0	70	61	1.4	16	14	0
2	245	1.37	69	58	65	31	55	24	37	3	41

Expt.	Products formed, grams									Sp. gr. of oil 20°/20°	Iodine number of oil
	CH_4	C_2H_6	C_3H_6	C_3H_8	C_4H_8	C_4H_{10}	C_5H_{10} and higher	CO_2	H_2O		
1	1.0	0.7	0.13	0.10	0.14	0.07	1.91	1.48	7.40	0.7041	116
2	2.0	45	0.88	0.22	1.15	0.17	3.70[a]	1.22	5.22[b]	0.7107	111

[a] This product contains 25% by volume of water-soluble material. [b] This product contains water-soluble organic material in large amount.

In order to show how the reaction of ethylene varied with its partial pressure and with the partial pressure of water gas present, the experiments recorded in Table III were performed. In comparing Expts. 1 and 2, it is noted that with lower partial pressure of water gas, the unsaturation of the product is increased and the total amount of reaction is less. The marked increase in oil yield when 22% of ethylene is added, keeping the partial pressure of water gas constant, is noted in comparing Expts. 2 and 3. The yield of oil in Expt. 4 is still large, even when the ethylene concentration is reduced to 12%, keeping the water-gas concentration constant. In fact, the yield of oil seems not to change rapidly in this concentration range with change in the ethylene concentration. The percentage of

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[15] See Frey and Yant, *Ind. Eng. Chem.*, 19, 492 (1927).

water-soluble organic material in the oil of Expts. 3 and 4 was not determined accurately, although it definitely contained some—probably around 5%. In Expt. 5, when the water-gas concentration is increased keeping the ethylene at 22%, an increase is noted in the amount of reaction over that obtained in Expt. 3, as evidenced by increased yields of oil, carbon dioxide and water. The striking thing in the comparison of Expts. 3 and 5, however, is the large increase in amount of water-soluble organic material as the concentration of water gas is increased. It should be pointed out that the presence of ethylene in the water gas largely increases the yield of hydrocarbons excluding the water-soluble organic material. This is evident from the data in Table III.

Table III

Data Showing the Dependence of the Reaction of Ethylene on Partial Pressure (250 Cc. of Catalyst)

Expt.	Temp., °C.	Flow rate, l./min.	Gas entering, liters				Composition in %			Gas leaving, liters			Gas converted, liters		
			H_2	CO	C_2H_4	N_2	Water gas	C_2H_4	N_2	H_2	CO	C_2H_4	H_2	CO	C_2H_4
1	211	1.10	118	103	0	0	100	0	0	108	94	0.2	10	9	0
2	210	1.24	53	44	0	149	39	0	61	46	38	0.2	7	6	0
3	213	1.31	53	41	54	95	38	22	40	16	37	21	37	4	33
4	213	1.27	56	40	31	122	39	12	50	21	34	5	35	6	26
5	206	1.29	82	58	49	34	62	22	15	41	49	14	41	9	35

	Products formed											
			Pentane and higher[b]									
Expt.	CH_4, l.	C_2H_6, l.	g.	g./l. H_2	g./l. CO	g./l. H_2 + CO	CO_2, g.	H_2O, g.	Sp. gr. of oil, 20°/20°	Iodine number of oil	Water-sol. comp. in oil, %
1	2.9	0.3	2.83	0.29	0.30	0.15	3.40	7.66	0.7155	79	0
2	2.5	..	1.68	.25	0.28	.13	1.33	4.44	.7129	94	0
3	2.6	28	5.67	.15	1.42	.14	2.18	4.82[a]	.7188	131	<8
4	1.8	24	5.57	.16	0.90	.13	1.98	5.86[a]	.7183	121	<8
5	3.1	30	5.76	.14	0.68	.12	2.96	6.78[a]	.7500	130	30

[a] These figures include some water-soluble organic material. [b] In the ethylene experiments these figures include some water-soluble organic material.

The results in Table III suggested that oxygen-containing organic material originally formed was being converted to hydrocarbons on the catalyst. Accordingly, the experiments recorded in Table IV were made. In these experiments a measured amount of a sample of our oil containing both hydrocarbons and oxygen compounds was passed over the catalyst in a stream of gas. The products were collected in the usual manner. In order to vaporize the heavier material the sample was finally heated to the temperature of boiling water while the gas was passing through. The liquid product collected after passage over the catalyst in no case contained appreciable amounts of water-soluble material. It was far less unsaturated than the original material. Probably, elimination of water from the oxygen-containing compounds had occurred, accompanied by combination of the unsaturated residues. Possibly some of the decrease in unsaturation is due to hydrogen retained on the catalyst surface. The presence of carbon monoxide possibly prevents combination of the unsaturated residues of the dehydration, resulting in a more unsaturated product. This is further evidenced by the appearance of ethylene in the gas in this case. No carbon dioxide appeared in the products, so that the carbon dioxide which always appears during the synthesis of hydrocarbons from water gas probably arises either in a way different from that in which the water does, or the elimination of carbon dioxide from intermediate products is so rapid that this type of intermediate compound does not persist.

TABLE IV

BEHAVIOR OF THE OXYGEN-CONTAINING COMPOUNDS WHEN CARRIED OVER THE CATALYST IN A GAS STREAM (250 CC. OF CATALYST)

Expt.	Temp., °C.	Gas used as carrier	Oil in— Cc.	W. S., %	I_2 no.
1	211	N_2	5.0	40	130
2	211	H_2	4.5	40	130
3	211	CO	4.5	40	130

Expt.	Gas leaving, liters CO	H_2	N_2	CH_4	C_2H_4	C_2H_6	Oil out Cc.	I_2 no.	H_2O formed, cc.
1	0.05	0.6	47.5	0.4	0	0.2	3.1	6	0.5
2	0.05	51.3	0	1.4	0	.18	2.2	6	.6
3	51.9	1.2	0	0.5	0.03	0	2.8	90	.7

It may be of interest to consider the effect on the reaction of varying ratios of H_2:CO. This is shown in Table V. Experiment 1 shows the use of ordinary water gas. As shown in Expt. 2, at approximately the same temperature an increase of hydrogen concentration causes a largely increased reaction which, however, results principally in methane formation. With approximately this same mixture, when the temperature is lowered as in Expt. 3, the methane formation is reduced but the oil yield is still only three-fourths of normal. When the hydrogen concentration is lowered with corresponding increase in the carbon monoxide concentration, very little reaction of any kind takes place. The oil in Expt. 2 is nearly saturated. However, in Expt. 4 a large decrease in the hydrogen concentration over that prevailing in Expt. 3 does not produce a corresponding unsaturation in the oil. The latter effect is doubtless to be attributed to the fact that the relatively large total consumption of hydrogen in Expt. 3 reduces the hydrogen concentration at the point where reaction is occurring. In Expt. 2, the slower rate as well as the high hydrogen concentration favors saturation of the product. The water layer from Expt. 4 was found to contain a small amount (about 0.5%) of acetone. This is the only case where the presence of acetone was definitely established in an experiment with a gas containing only carbon monoxide and hydrogen on a cobalt catalyst.

TABLE V

EFFECT ON THE REACTION OF VARYING RATIOS OF H_2 : CO (250 CC. OF CATALYST)

Expt.	Temp., °C.	Flow rate, l./min.	Entering gas, liters		Composition of entering gas, %		Gas leaving, liters		Gas converted, liters	
			H_2	CO	H_2	CO	H_2	CO	H_2	CO
1	225	1.28	123	107	54	42	108	94	15	14
2	220	1.06	115	28	77	19	52	0.7	63	28
3	207	1.25	185	53	75	22	170	42	15	11
4	207	1.13	50	172	22	77	47	164	3	8

	Products formed										
Expt.	CH_4, g.	C_2H_4 g.	C_2H_6, g.	Pentane and higher g.	g./l. H_2	g./l. CO	g./l. H_2 + CO	CO_2, g.	H_2O, g.	Sp. gr. of oil, 20°/20°	Iodine number of oil
1	...	...	..	3.94	0.26	0.29	0.14	2.62	9.02	0.7182	88
2	16.7	0.02	1.14	0.98	.16	.036	.011	10.21	18.6	.7098	4
3	3.8	.52	0.12	3.00	.20	.29	.12	1.18	7.87	.7090	64
4	1.0	.15	..	0.7	.2	.1	.07	1.15	3.00	...	79

Experimental Results Using Cobalt–Copper Catalyst.—Cobalt–copper catalysts were prepared by the same general method that was used in preparing the cobalt–copper–manganese oxide catalyst. They showed no striking differences in behavior except that they were somewhat less active. It is thought, however, that their activity could be increased by improvements in the method of preparation. In general, a somewhat lighter oil and more carbon dioxide relative to water were produced.

Experimental Results Using Iron–Copper Catalyst.—From the practical standpoint we have found the iron–copper catalysts to be the most satisfactory we have used. When properly prepared they are very hard and strong, relatively insensitive to overheating and produce little or no methane in spite of the fact that the temperature required is 30–40° higher than is necessary for the same conversion with cobalt–copper–manganese oxide catalysts.

Catalyst Preparation.—A hot solution of ferric and copper nitrates, in which the atomic ratio Fe : Cu was 4:1, was precipitated by slowly stirring in a solution of sodium hydroxide. The precipitate was thoroughly washed by decantation until it began to become colloidal. It was then dried very slowly until it started to form a gel which was of suitable consistency for molding by forcing through a grease gun. The molded material was then dried slowly up to a final temperature of 200°, at which point it shows a metallic luster and fracture. It was then very slowly reduced in place by a mixture of hydrogen and nitrogen at 150°, gradually increasing the partial pressure of hydrogen and the temperature until finally pure hydrogen was used at 285°. The reduced material is pyrophoric and its hardness is decreased by the rapid oxidation which takes place upon exposure to air. It is necessary to avoid the presence of chlorides since they are very difficult to wash out of ferric hydroxide precipitates and if allowed to remain, according to our experience, reduce the activity of the resulting catalyst. Probably some small amount of alkali is retained in the catalyst. The effect of this is not definitely known.

Results obtained with the iron–copper catalyst are shown in Table VI. The extremely small amount of methane produced is to be noted as well as the small amounts of the intermediate hydrocarbon fraction and, in contrast to results with cobalt catalysts, the great preponderance of carbon dioxide over water.

TABLE VI

RESULTS OBTAINED WITH TWO PREPARATIONS OF IRON–COPPER CATALYST[a] (200 CC. OF CATALYST)

Expt.	Temp., °C.	Flow rate, l./min.	Gas entering, liters		Gas leaving, liters		Gas converted, liters	
			H_2	CO	H_2	CO	H_2	CO
1	256	1.23	142	125	124	93	18	32
2	266	1.16	129	94	104	50	25	44

	Products formed							
	Methane[b]				Ethylene			
Expt.	g.	g./l. H_2	g./l. CO	g./l. $H_2 + CO$	g.	g./l. H_2	g./l. CO	g./l. $H_2 + CO$
1	0.82	0.045	0.026	0.016	1.26	0.068	0.039	0.025
2	Too small to detect				1.39	.057	.031	.020

	Products formed							
	Ethane				Pentane and higher			
Expt.	g.	g./l. H_2	g./l. CO	g./l. $H_2 + CO$	g.	g./l. H_2	g./l. CO	g./l. $H_2 + CO$
1	1.49	0.081	0.046	0.030	5.78	0.31	0.18	0.11
2	1.36	.055	.031	.020	8.37	.34	.19	.12

	Products formed			
Expt.	CO_2 (g.)	H_2O (g.)	Sp. gr. of oil 20°/20°	Iodine number of oil
1	35.6	3.1	0.7294	106
2	48.0	2.7	.7340	119

[a] The amount of the intermediate hydrocarbon fraction was too small to analyze accurately. [b] The results for methane are not very accurate on account of the small amounts obtained and on account of the presence of small amounts of methane in the water gas used.

In experiments in which the water gas contained ethylene, it was found that the ethylene did not enter into reaction at all and that no oxygen-containing compounds were obtained. This indicates that if intermediate, oxygen-containing compounds are formed, they are quickly decomposed to produce hydrocarbons, as was suggested for compounds which tend to eliminate carbon dioxide, in connection with the results on cobalt catalysts. However, it seems here that the mechanism of hydrocarbon formation differs essentially from that obtaining on cobalt catalysts in that ethylene does not increase the yield of oil. The small quantities of methane formed here, considered with respect to the considerably larger amounts formed on the cobalt catalyst and the methane formed when the oxygen-containing compounds decompose on the cobalt catalysts, suggest that the methane formation always noted with the cobalt catalyst arises during the dehydration of these oxygen-containing compounds. Some of the differences in behavior of cobalt and iron catalysts may be due, of course, to the difference in temperature—particularly some of the difference in the ratio CO_2:H_2O, since this has been shown to increase with increased temperature on the cobalt catalyst.

With the iron–copper catalysts used here, the oil formed was heavier than that obtained with cobalt catalysts. It contained about 3% of very heavy hydrocarbons insoluble in acetone. The product from the cobalt catalysts contained none of these.

Experiments Using Iron–Copper–Manganese Oxide Catalysts.—Catalysts consisting of iron, copper and manganese oxide were prepared by the same general method used for the iron–copper catalysts. The activity of the catalyst, its physical properties and its action were quite similar to those of the iron–copper catalyst. One point of interest was a test made on its susceptibility to poisoning. Short tests failed to show any poisoning action when using water gas from which hydrogen sulfide had been removed but which retained its original content of organic sulfur.

Nature of the Oxygen-Containing Compounds Formed on Cobalt Catalysts When Using Water Gas Containing Ethylene.—Only recently have we obtained larger quantities of the oxygen-containing compounds formed from water gas–ethylene mixtures on cobalt catalysts. A careful examination of this product should be made. As yet we have only the following qualitative observations: aldehydes and alcohols are present; methyl alcohol, acids, esters and acetone are not present; the whole product boils below 100°. Boiling points of the pure constituents cannot be deduced from this latter fact since constant boiling mixtures are doubtless formed.

Discussion of Results

The work presented in this paper shows that cracking of the heavier hydrocarbons does not play any considerable part in the formation of the mixture of hydrocarbons higher than methane, when the synthesis is carried out on a cobalt–copper–manganese oxide catalyst under the conditions described. The experiments in which acetone was passed over the catalyst with hydrogen, nitrogen or carbon monoxide indicate that acetone likewise is not a predominating intermediate. Acetone is almost never present in the products from water gas alone. Polymerization of ethylene or of higher olefins does not occur.

Ethylene, at least in concentrations over 10%, enters into reaction upon the cobalt–copper–manganese oxide catalyst in the presence of water gas, forming higher hydrocarbons and large quantities of oxygen-containing compounds. The oxygen-containing compounds dehydrate to a greater or less extent, producing hydrocarbons. The dehydration is accompanied by some polymerization. The extent to which ethylene enters into these reactions does not change largely with the ethylene concentration when this is above about 10%, but the formation of these intermediate products depends quite markedly upon the concentration of water gas. These facts make it seem likely that these oxygen-containing compounds form the intermediate products in the synthesis of hydrocarbons under these conditions from water gas which does not contain added ethylene. Similar experiments with still lower concentrations of ethylene would be desirable. We have not yet determined whether the higher olefins act similarly to ethylene, but presumably they do, to some extent at least. The mechanism by which the hydrocarbons are formed may be regarded as follows. There is some association of hydrogen and carbon monoxide on the catalyst surface. This complex may either decompose, giving an olefin and water, or ethylene or other olefin may combine with it to form an oxygen-containing compound which may either pass into the products or eliminate water to form a higher olefin hydrocarbon. The olefins are to be regarded as the primary hydrocarbon products. They may later be hydrogenated to form paraffin hydrocarbons or pass on into the products, depending upon the experimental conditions of hydrogen concentration, space velocity, catalyst and temperature.

The mechanism of the reactions on the iron catalyst is essentially different from that on the cobalt catalyst, aside from the fact that carbon dioxide is predominant instead of water, since ethylene does not enter into the reaction in this case. The extremely small amounts of methane ordinarily formed on iron–copper catalysts in contrast to the appreciable amounts from the cobalt catalyst (which may quite likely arise during dehydration of the intermediate oxygen compounds in this case) also suggest a different mechanism. It is possible that further experiments with iron–copper catalysts at lower temperatures or higher space velocities may permit isolation of some intermediate product.

Summary

1. It has been shown that in mixture with carbon monoxide and hydrogen, ethylene reacts on a cobalt–copper–manganese oxide catalyst to form large quantities of higher hydrocarbons and oxygen-containing compounds. The latter may dehydrate to form hydrocarbons. The dehydration may be accompanied by polymerization. Alone, or with either carbon monoxide or hydrogen, ethylene does not form higher hydrocarbons under the conditions described. The cracking of heavy hydrocarbons does not form a considerable part of the process. Acetone is not an important intermediate product. The higher olefins do not polymerize under these experimental conditions.

2. The mechanism of hydrocarbon formation on an iron–copper catalyst is essentially different from that on a cobalt–copper–manganese oxide catalyst, aside from the relative amounts of carbon dioxide and water formed, since in this case ethylene does not enter into reaction.

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