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RECENT INVESTIGATIONS ON IRON CATALYSTS

INTRODUCTION

During the years 1925 to 1928, numerous investigations were carried out with cobalt and nickel. At the same time, we also tried to find effective and lasting iron catalysts which eventually might be used to replace the expensive cobalt in large technical enterprises. A summary of the results obtained during those years is presented in Die Erdolsynthese (34). In the following, a short resume of this work is given.

The highest yields obtained with iron catalysts at that time were 35 to 45 grams of liquid hydrocarbons per cubic meter of water gas. The catalysts contained iron and copper in the ratio of 4:1 and were prepared by decomposing the nitrates. Some additional constituents were added which were believed to be favorable and increase the activity. We used sodium-glass powder and sodium aluminate of composition $1Al(OH)_3$-1/3NaOH. The additional constituents amounted to 10 percent and were mixed in dry form with the finished iron-copper oxide mixture. The catalysts mentioned were tested with water gas. The time for which the catalysts remained active was not very long. We conducted a laboratory experiment and used 40 grams of oxides (corresponding to approximately 22 grams of Fe); the gas-flow velocity was 4 liters per hour. In later experiments we used 10 grams of iron most of the time. Hence, for the earlier runs, the quantity of catalyst was more than twice as large for the same gas velocity. This has to be taken into consideration when the efficiency of those early catalysts is judged. For this reason, direct comparison between the yields at that time with the yields obtained at present is not immediately possible. This is complicated also by the fact that our present results are not based on water gas but instead are referred to mixed gas ($29CO + 58H_2$). It is conceivable that iron catalysts will give better yields with water gas than with mixed gas.

The best catalyst used at that time consisted of 4Fe + 1Cu + 10 percent sodium aluminate ($1Al(OH)_3 + 1/3NaOH$). The preparation of this catalyst was carried out under the conditions mentioned earlier. With 44 grams of catalyst (corresponding to approximately 22 grams of iron) and a gas velocity of 4 liters per hour using water gas, a maximum yield of 44 grams per cubic meter was obtained. The highest efficiency was reached after the catalyst was in operation for 5 days. After 14 days of operation, the yield still amounted to 38 grams. Between the 14th and 18th days of operation, the activity decreased very rapidly from 33 to 21 percent contraction.

During 1928 and 1929, the investigations with iron catalysts were resumed (A. Hintermaier). The object was to reach the same degree of perfection with iron catalysts as had been reached with cobalt catalysts. At that time, we investigated, among others, Fe-Cu-MnO catalysts which contained 40 percent silica-gel powder mixed with the catalyst in the dry state. A definite improvement as compared to the earlier Fe-Cu catalysts could not be observed at this time. However, we calculated a yield of 48 grams per cubic meter for water gas at 250°C. when the gas rate was 4 liters of gas per hour and the catalyst consisted of Fe-Cu-Mn + 40 percent of silica gel. The catalyst contained a total of 4 grams of iron (Fe:Cu:Mn = 4:1:1). The life of this catalyst was very short, however.

During 20 to 25 hours of operation, the contraction decreased by one-third. At the same time, the products formed showed a distinct yellowish tinge. Only for a short period of operation (approximately 20 hours) did the catalyst come up to expectations and produce a yield comparable to the calculated yield.

For the following experiments Fe-Cu-2-component and Fe-Cu-MnO-3-component catalysts were chiefly used. For the experiments that used Fe-Cu, the catalysts were formed largely from ferrous compounds. The Fe-Cu-MnO-3-component catalysts were formed from ferric nitrate exclusively. For the sake of clarity these two catalyst species are dealt with separately. In the course of the experiments, it was found that iron could give good results when used alone under certain experimental conditions. These Fe-1-component experiments are described in the section on "Copper-free Iron Catalysts".

IRON-COPPER CATALYSTS FROM FERROUS COMPOUNDS

In the following, those results are first described that were obtained with iron-copper catalysts produced by precipitation of various ferrous compounds under various conditions. The ferrous compounds were made by dissolving iron shavings in various acids; in some other cases, the ferrous compounds were bought as such, for example, iron-II-sulfate and iron-II-chloride.

After some experiments which promised little success and were carried out with copper-free ferrous carbonate catalysts (on which we shall report later in more detail), the same catalysts were investigated, containing 20 percent of copper. The conditions for preparation were the same as those of the copper-free catalysts. Therefore, we refer to what has been said about the preparation of copper-free catalysts.

Dissolving Iron Metal in Formic Acid and Precipitation with Sodium Bicarbonate

Iron shavings were dissolved in dilute formic acid, and the resulting iron-formate solution was precipitated in the cold with sodium bicarbonate and in the presence of copper nitrate (20 percent of copper). The catalyst was washed in a CO_2 atmosphere to avoid oxidation of ferrous carbonate to ferric hydroxide. The catalyst was dried in vacuo at room temperature. For investigating the activity we always used 10 grams of iron and 2 grams of copper. The flow velocity of the mixed gas, which consisted of 29 percent CO and 58 percent H_2, was 4 liters per hour. The catalysts were taken into operation without any previous pretreatment.

Since addition of manganese to iron-copper catalysts produced from ferrous compounds activated them more or less, corresponding to production conditions, we investigated the effect of alkalization of the manganese on activity. We found that alkalization of the manganese did not improve the efficiency of the catalyst. For the sake of clarity, we discussed the influence of manganese and some other additions to the ferrous catalysts in the same place where we discussed the iron-copper catalysts without additions.

Table 48.—Activity of Ferrous catalysts containing copper (From ferrous formate by precipitation with sodium bicarbonate)

Composition of catalyst	Preparation conditions	Temperature, °C.	Maximum contraction		Maximum yields, grams per cubic meter of mixed gas
			Percent	Days	
5Fe-1Cu	Ferrous formate and copper nitrate precipitated in the cold with $NaHCO_3$	238	25	2	39
5Fe-1Cu	Ferrous formate and copper nitrate precipitated in the cold with $NaHCO_3$	235	26	3	40
5Fe-1Cu + 10% basic $MgCO_3$	Ferrous formate and copper nitrate precipitated in the cold with $NaHCO_3$, basic $MgCO_3$ mixed in dry	235	27	3	47
5Fe-1Cu-1/4Al	Precipitation with $NaHCO_3$ (simultaneous)	235	23	5	43
5Fe-1Cu-1Mn	Precipitation with $NaHCO_3$ (simultaneous)	237	26	4	48(?)

Table 48 contains results obtained from some catalysts prepared by the mentioned methods. With an iron-copper catalyst containing iron and copper in the ratio of 5:1 (first experiment), 39 grams of liquid products were obtained per normal cubic meter of mixed gas at a maximum contraction of 25 percent. Catalyst 2 differs from catalyst 1 in that it was not dried at room temperature in vacuo, but instead in air at 105°C. Thus, the ferrous iron was partly oxidized to ferric iron. This can be followed easily by the change in color from greenish-gray to brown. The efficiency of this catalyst was the same as that of catalyst 1. For this reason, in our future experiments we no longer resorted to drying in vacuo.

After mixing the 5Fe-1Cu catalyst with 10 percent basic magnesium carbonate (mixed dry), the yield could be increased to 47 grams (third experiment). With an addition of 5 percent aluminum (simultaneous precipitation of the three components) 43 grams of liquid products were obtained (fourth experiment). A catalyst consisting of 5Fe-1Cu, containing 20 percent of manganese, for which the components were precipitated simultaneously with sodium bicarbonate, a yield of 48 grams was obtained.

Precipitation from Salts with Sodium Carbonate without Alkalization Thereafter

To simplify the preparation, we used iron-II-sulfate as starting material instead of iron-II-chloride. These catalysts were precipitated in the cold with sodium carbonate in the presence of copper nitrate.

Table 49.—Activity of iron catalysts containing copper (Prepared from $FeSO_4$ and $FeCl_2$ by precipitation with Na_2CO_3)

Experiment No.	Composition of catalyst	Preparation conditions	Temperature, °C.	Maximum contraction Percent	Maximum contraction Days	Maximum yields, grams per cubic meter of mixed gas
1	5Fe-1Cu	$FeSO_4$ and $Cu(NO_3)_2$ precipitated in the cold with Na_2CO_3	242	14	6	14
2	5Fe-1Cu	$FeSO_4$ and $Cu(NO_3)_2$ precipitated in the cold with Na_2CO_3	250	23	5	25
3	5Fe-1Cu-1Mn	$FeSO_4$, Cu-Mn nitrate precipitated in the cold with Na_2CO_3	240	14	4	22
4	5Fe-1Cu-1Mn	$FeCl_2$, Cu-Mn nitrate precipitated in the cold with Na_2CO_3	240	22	3	32
5	5Fe-1Cu-1Mn	$FeCl_2$, Cu-Mn nitrate precipitated in the cold with Na_2CO_3	235	20	4	30
6	5Fe-1Cu-1Mn	$FeCl_2$, Cu-Mn nitrate precipitated in the cold with Na_2CO_3, catalyst extracted for 24 hours with water	235	12	4	18

Experiments 1 and 2 (table 49) show that the efficiency of the catalyst produced from iron sulfate is lower than that of the catalysts produced from ferrous formate. The yield amounted only to 14 grams per cubic meter of mixed gas at 242°C. and only 25 grams per cubic meter of mixed gas at 250°C. An addition of 20 percent of manganese at 242°C. furnished 22 grams of liquid products (experiment 3). When $FeCl_2$ was used instead of $FeSO_4$, this yield increased to 32 grams (experiment 4). When the experiment was repeated, 30 grams were obtained at a temperature of 235°C. (experiment 5).

We believed at first that the poor activity of the catalysts produced from $FeSO_4$ and $FeCl_2$ could be attributed to the presence of some Na_2SO_4 and NaCl, respectively. For this reason, catalyst 5 was washed for 24 hours with water to remove the last traces of the sodium salts before it was used for the operation proper. The wash water contained definite quantities of chloride ions. Experiment 6 shows that this extracted catalyst does not work any better than the unextracted catalyst; in fact, it was found that the extracted catalyst was less active than the unextracted. The same effect was observed when a catalyst was precipitated with potassium carbonate. In this case, the catalyst activity did not improve by washing either, as could be seen by comparing it with a similar unwashed catalyst. The explanation for this behavior is possibly as follows: Earlier investigations have shown that iron catalysts may be activated considerably by the addition of small quantities of alkali. After the normal washing-out operation following the precipitation with soda, there are certainly some traces of alkali left in the catalyst that could cause activation of the contact. By a further washing operation (extraction) with water, the alkali content is reduced so considerably that it is no longer sufficient for an activation. Therefore, the extracted catalyst cannot normally reach the activity of the unextracted catalyst. Experiment 6 confirms this.

Furthermore, the alkali remaining in the catalyst after a normal washing operation may not produce sufficient activation simply because it is combined with chlorine. This would serve as an explanation for the low activity of catalysts prepared from $FeSO_4$ and $FeCl_2$, respectively. A more efficient catalyst was not obtained either when the catalyst precipitated with soda was boiled three times with a soda solution before extraction. One is forced to assume, therefore, that only an alkali addition to the finished catalyst can increase the activity in the desired measure. That this is actually the case may be seen from the experiments described in the following section.

Influence of a Separate K_2CO_3 Addition

We used potassium carbonate as an alkalizing agent. At first, the quantity was 1/2 percent referred to the iron metal. The alkalization was carried out in such a way that the catalyst already dried at 105°C. was impregnated with a potassium carbonate solution. It was then dried on the sand bath with a small flame.

From table 50 the activating influence of the potassium carbonate addition may easily be noticed. Catalyst 1 was precipitated from a ferrous sulfate solution containing copper and manganese nitrate (precipitating agent, soda, and precipitation carried out in the cold) and furnished a maximum contraction of 14 percent without the extra addition of K_2CO_3. The yield amounted to 22 grams of liquid products per cubic meter of mixed gas (experiment 1). When 1/2 percent K_2CO_3 was added to the same catalyst, the yield was doubled (experiment 2). The optimum reaction temperature could be lowered from 240°C. (experimental) to 230°C. Experiments 3 and 4 give the results with catalysts of identical composition which, however, were precipitated from an $FeCl_2$ solution instead of an $FeSO_4$ solution. A later activation with 1/2 percent K_2CO_3 increased the yield from 32 to 48 grams. When the precipitation was carried out with sodium bicarbonate instead of soda, the yield was 45 grams (experiment 5). The use of sodium bicarbonate as precipitating agent, therefore, does not seem to give any advantages. From experiment 6 it can be observed that a catalyst produced from ferric nitrate as a starting material gives a catalyst of lower activity (for the same conditions of preparation). A catalyst obtained by thermal decomposition of the nitrates and impregnated with 1/2 percent K_2CO_3 was far inferior to the precipitated catalysts (experiment 7). Iron-copper-manganese catalysts which were precipitated with soda at the boiling point and contained 1/2 percent K_2CO_3 gave 51 grams of liquid products at 230°C. (experiment 8). We discovered that the washing time may be shortened considerably for a catalyst that was precipitated from a hot solution. For this reason, we always resorted to this kind of precipitation in our future work.

The results up to this time refer to catalysts which contained copper and manganese, precipitated from their nitrates. From experiment 10, it may be observed that the chlorides of the promoters Mn and Cu may be used with success also. To investigate whether the addition of Mn to the already alkalized catalysts causes a further increase in activity, manganese-free catalysts were tested during experiments 11 and 12. It is evident from the experiments that a subsequent alkalization of an iron-copper catalyst without manganese gives a yield of 50 grams. The catalyst which was not alkalized with 1/2 percent potassium carbonate in comparison with the previous catalyst, yielded only 35 grams of liquid products. Experiments 13 and 14 finally disclose that the addition of magnesium (simultaneous precipitation of the chlorides) reduces the activity of the 5Fe-1Cu catalyst.

Table 50.—Influence of adding potassium carbonate

Experiment No.	Composition of catalyst	Mode of preparation	K_2CO_3 contents referred to iron, percent	Temperature, °C.	Maximum contraction, percent	Maximum yields, grams per cubic meter of mixed gas
1	5Fe-1Cu-1Mn	$FeSO_4$, Cu- and Mn-nitrate precipitated in the cold with Na_2CO_3	0	240	14	22
2	5Fe-1Cu-1Mn	$FeSO_4$, Cu- and Mn-nitrate precipitated in the cold with Na_2CO_3	1/2	230	29	43
3	5Fe-1Cu-1Mn	$FeCl_2$, Cu- and Mn-nitrate precipitated in the cold with Na_2CO_3	0	240	22	32
4	5Fe-1Cu-1Mn	$FeCl_2$, Cu- and Mn-nitrate precipitated in the cold with Na_2CO_3	1/2	230	30	48
5	5Fe-1Cu-1Mn	$FeCl_2$, Cu- and Mn-nitrate precipitated with $NaHCO_3$	1/2	232	28	45
6	5Fe-1Cu-1Mn	$Fe(NO_3)_3$, Cu- and Mn-nitrate precipitated with Na_2CO_3	1/2	232	25	35
7	5Fe-1Cu-1Mn	Fe-Cu-Mn-nitrate thermally decomposed	1/2	232	17	24
8	5Fe-1Cu-1Mn	$FeCl_2$, Cu- and Mn-nitrate precipitated hot with Na_2CO_3	1/2	230	32	51
9	5Fe-1Cu-1Mn	$FeCl_2$, Cu- and Mn-nitrate precipitated hot with Na_2CO_3	0	240	23	40
10	5Fe-1Cu-1Mn	$FeCl_2$, $CuCl_2$, and $MnCl_2$ precipitated hot with Na_2CO_3	1/2	233	30	50
11	5Fe-1Cu	$FeCl_2$, $CuCl_2$ precipitated hot with Na_2CO_3	1/2	235	30	50
12	5Fe-1Cu	$FeCl_2$, $CuCl_2$ precipitated hot with Na_2CO_3	0	235	22	35
13	5Fe-1Cu-1/2 Mg	$FeCl_2$, $CuCl_2$, $MgCl_2$ precipitated with Na_2CO_3	1/2	235	23	37
14	5Fe-1Cu-1Mg	$FeCl_2$, $CuCl_2$, $MgCl_2$ precipitated with Na_2CO_3	1/2	235	21	33

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The optimum K_2CO_3 content lies between 1/4 and 1/8 percent. The yields of liquid hydrocarbons amounted to 53 grams per cubic meter of mixed gas, whereas the other catalyst (comparative catalyst) containing 1/2 percent K_2CO_3 yielded only 50 grams. The time of induction for the catalyst to reach maximum activity was 1 to 2 days for 1/4 to 1/8 percent K_2CO_3 and 3 days for 1/16 percent. It has proved beneficial to start the catalyst off at first at a temperature of 235°C. As soon as the contraction has reached 25 to 30 percent, the temperature may be lowered to 228° to 230°C., in some cases even to 225°C., without changing the catalyst activity noticeably.

Table 51.—Influence of quantity of K_2CO_3 upon activity of 5Fe-1Cu catalysts

Experiment No.	K_2CO_3 content, percent	Temperature, °C.	Maximum contraction, percent	Maximum yields, grams per cubic meter of mixed gas	Contraction Percent	Contraction Days
1	0	230	21	37	20	42
2	1/16	230	30	53	28	42
3	1/8	230	31	56	26	42
4	1/4	228	31	56	26	42
5	1/2	228	30	50	18	21
					7	32
6	1	228	29	28	6	9
7	2	228	22	—	7	4

Besides causing a better yield, the addition of small quantities of K_2CO_3 exerts a favorable influence upon the life of the catalyst. The last column of table 51 shows the contraction as still obtained after a certain length of operation. The catalysts with 1/16, 1/8, and 1/4 percent K_2CO_3 contents still gave a contraction of 28 to 26 percent after 40 days of operation, whereas a comparative catalyst with 1/2 percent K_2CO_3 only furnished 18-percent contraction after 21 days of operation and 7 percent contraction after 32 days. With the addition of 1 percent K_2CO_3, the activity is expected to decrease even faster, but a contraction of 29 percent was still obtained; after 6 days only 20-percent and after 9 days only 6-percent contraction was measured (experiment 6). The activity of a catalyst containing 2 percent K_2CO_3 was such that within 4 days the contraction decreased from 22 to 7 percent. The life of a catalyst that was not subsequently alkalized (experiment 1) is quite good, too; however, the maximum yield was only 37 grams and is only obtained after operating for 14 days. After 40 days of operation the maximum contraction of 21 percent, once reached, remained practically unchanged.

Table 52.—Influence of quantity of K_2CO_3 upon life of catalyst (5Fe-1Cu catalyst)

Experiment No.	K_2CO_3 content, percent	Yields, grams per cubic meter of mixed gas after the following days: 7	14	21	28	35	42	49	56
1	0	26	37	—	—	34	—	35	—
2	1/16	53	53	53	49	48	47	43	32
3	1/8	56	55	56	52	47	45	38	25
4	1/4	56	56	52	49	46	37	32	28
5	1/2	50	45	37	21	12	—	—	—

Table 52 shows very explicitly the favorable influence that small K_2CO_3 quantities (varying from 1/16 to 1/4 percent) have upon the life of the catalyst. In this table the yields of liquid products are recorded with increasing time of operation. After 42 days of uninterrupted operation with a catalyst containing 1/16 percent K_2CO_3, 47 grams of liquid products per cubic meter of mixed gas still were obtained; with a catalyst containing 1/8 percent K_2CO_3, 45 grams; and with another catalyst containing 1/4 percent K_2CO_3, 37 grams of liquid products per cubic meter of mixed gas were formed. The average yield for 6 months is approximately 50 grams per cubic meter of mixed gas for all of these catalysts. It should be remembered that the recorded yields were not referred to standard conditions (0°C., 760 mm.). By referring to normal conditions, the yields seemed higher by about 10 percent. These data were compared with the yields obtained from a catalyst containing 1/2 percent K_2CO_3. We found that this catalyst (containing 1/2 percent K_2CO_3) gave very much lower yields after 21 days. Thus, we found that the yield after 21 days was only 37 grams, and after 35 days it had decreased to 12 grams. The catalyst that was not treated with K_2CO_3 gave a maximum of 37 grams of liquid products after 14 days of operation. The activity from there on remained constant; after 49 days, 35 grams of liquid products were still obtained.

A repetition of the experiments with smaller additions of K_2CO_3 showed that the maximum yields and the stability of the catalysts were reproducible.

Table 53.--Influence of quantity of K_2CO_3 and length of operation upon the ratio, yield:contraction

Experiment No.	K_2CO_3 content, percent	Operation, days	Contraction, percent	Yields, grams per cubic meter	Yield:contraction, after days 7	14	21	28	35
1	0	7	13	26	2.0	1.95	—	—	1.62
2	1/16	7	28	53	1.9	1.8	1.8	1.75	1.64
3	1/8	7	30	56	1.87	1.83	1.83	1.73	1.65
4	1/4	7	29.5	56	1.9	1.9	1.72	1.66	1.64
5	1/2	7	27.5	50	1.8	1.8	1.7	1.6	1.57

From table 52 it appears that the 5Fe-1Cu catalyst containing 1/16 percent K_2CO_3 still exhibits a somewhat higher activity after 6 to 7 weeks of operation than the corresponding catalyst containing 1/8 percent K_2CO_3. However, after 8 weeks the yields are approximately the same in both cases. It appears that the activity of the catalysts containing 1/8 and 1/4 percent K_2CO_3 is higher during the first weeks of operation than that of the other catalysts; that is, these catalysts require a shorter time of induction.

To find out whether there is a relationship between the yield and contraction, table 53 shows the ratio of yield:contraction for catalysts containing varying amounts of K_2CO_3.

After 7 days of operation, the value of the ratio of yield:contraction varies between 1.8 and 2.0 for all the catalysts concerned. The highest value of 2.0 refers to the K_2CO_3-free catalyst. The lowest value, 1.8, refers to the catalyst containing the greatest amount of K_2CO_3. With increasing time of operation, the ratio of yield:contraction decreases rather rapidly for all the catalysts, and after 6 weeks it reaches a value of 1.57 to 1.65. This means that in the course of the operation gaseous products form at the expense of liquid hydrocarbons. The increasing formation of gaseous hydrocarbons with increasing time of operation may also be observed from analysis of the reaction gases. Thus, we found that a 5Fe-1Cu catalyst containing 1/4 percent K_2CO_3 only yielded 3.4 volume percent of gaseous hydrocarbons after 8 days; however, after 6 weeks of operation, the quantity of gaseous hydrocarbons nearly doubled, although the CO was not converted to as large an extent as at the beginning of the operation.

Influence of Mode of Alkalization Upon Reaction

Up to now the K_2CO_3 addition had been undertaken after the catalyst has been dried. The catalyst was mixed with the K_2CO_3 solution to form a heavy paste, then dried carefully on the sand bath. We have also mixed the moist catalyst paste (as obtained after washing) with the K_2CO_3 solution and dried the mass at 105°C. We found that this mode of addition does not affect the characteristics of the catalyst to any noticeable degree. This may be seen from experiments 1 and 2 in table 54. In both cases, the maximum yield was 57 grams of liquid products, and the average yield for 4 weeks of operation was 52 grams.

Table 54.—Influence of mode of alkali addition (5Fe-1Cu catalyst)

Experiment No.	K_2CO_3 content, percent	Conditions of preparation	Temperature, °C.	Maximum Contraction, percent	Maximum yields, grams per cubic meter of mixed gas	Average yield Grams per cubic meter	Average yield Days
1	1/4	Dry catalyst impregnated with K_2CO_3	229	30	57	52	28
2	1/4	Moist paste mixed with K_2CO_3	229	31	57	52	28
3	1	Moist paste mixed with K_2CO_3 and washed twice	229	14	26	--	--
4	1/4	Washed 9 times before impregnation with K_2CO_3	229	30	58	--	--

We also have added 1 percent K_2CO_3 to a wet catalyst; then we washed the resulting mixture twice with water through a filter funnel. This catalyst behaved just like a catalyst that was not alkalized at all and gave 26 grams of liquid products (experiment 3) at a contraction of 14 percent. The minimum quantity of K_2CO_3 required for proper activation had therefore been removed from the catalyst by the washing operation.

In the case of experiment 4, the catalyst was not washed six times, as was usually done but was washed nine times instead and then impregnated with 1/4 percent K_2CO_3. Since its activity was no better than that of a catalyst which was washed only six times, we are justified in assuming that it is sufficient to wash the catalyst only six times.

Influence of Shaping

In the following course of the investigation, we have analyzed what effect shaping has upon the iron catalysts. We have used a catalyst in powder form in the laboratory. On a large scale, however, the synthesis may only be carried out with a catalyst having a definite form. When the dried catalyst is broken into little pieces, they do not have sufficient rigidity to be used successfully. However, it is possible to produce small pellets by protruding the wet catalyst through small holes. These pellets exhibit excellent mechanical properties. Furthermore, we succeeded in getting a catalyst of good mechanical properties by adding 10 percent of starch (35) (referred to iron metal). The activity of these catalysts may be observed from table 55. For the sake of comparison, the results obtained with this catalyst are compared with those of a powdered catalyst of the same composition.

Table 55.—Influence of shape
(5Fe-1Cu catalyst containing 1/4 percent K_2CO_3)

Exp. No.	Conditions of preparation	Exp. Temp., °C.	Max. contraction, percent	Average yield, grams/cubic meter, mixed gas 7 days	14 days	28 days
1	Catalyst used as a powder.	229	31	58	58	52
2	Catalyst containing 10% starch.	229	31	59	59	53
3	Catalyst pelleted.	229	31	57	56	46

All three catalysts furnished approximately the same yield of liquid products during the first 14 days of operation. After 28 days of operation, we observed that the activity of the powdered catalyst and that of the catalyst containing starch were still approximately equal (average yield, 52 and 53 grams, respectively), but the activity of the pelleted catalyst decreased somewhat more rapidly. In the latter case, the average yield after 4 weeks of operation was about 46 grams. The somewhat faster decrease in activity of the pelleted catalyst may be attributed to overheating, which is liable to occur more readily with pellets than with a powder. The average apparent density of the pelleted catalyst was 0.95, whereas the average apparent density of the powdered catalyst and of that catalyst containing starch was only about 0.6 in both cases.

Influence of Addition of Na_2CO_3

After we had investigated the effect of the addition of K_2CO_3 upon the activity and the life of the precipitated iron-copper catalysts (produced from ferrous iron), we also investigated the effect of a subsequent addition of Na_2CO_3. From earlier experiments we know that Na_2CO_3, as well as K_2CO_3, is capable of increasing the activity of iron-copper catalysts which were produced by decomposing the nitrates. The increased activity resulting from the addition of Na_2CO_3 was not quite as pronounced as the increase in activity from K_2CO_3; however, (36) the life of the catalysts containing Na_2CO_3 was longer than that of the catalyst containing K_2CO_3.

Table 56.—Influence of subsequent addition of Na_2CO_3
(Catalyst composition 5Fe-1Cu)

Experiment No.	Na_2CO_3 content, percent	Yield, grams per cubic meter of mixed gas, in days 8	12	19	30	38
1	1/4	50	54	49	45	42
2	1/2	54	55	50	43	37
3	1	47	40	31	16	—
4	2	20	10	—	—	—

Table 56 shows the results with a 5Fe-1Cu catalyst prepared by precipitating a mixture of ferrous chloride with Na_2CO_3. After the precipitation, 1/4, 1/2, 1, and 2 percent of Na_2CO_3 was added. With 1/4 percent of Na_2CO_3, a maximum yield of 54 grams was obtained after approximately 12 days of operation (experiment 1). When this catalyst was compared to one containing 1/4 percent K_2CO_3, it was observed that the percent contraction increased at a much slower rate for a catalyst containing Na_2CO_3. If the yields and the life are just as good as in the case of a K_2CO_3 catalyst, it is preferable to use K_2CO_3 as a promoter, especially since it is possible to regenerate the K_2CO_3-containing catalysts with greater assurance and safety. We shall report on that later.

The catalyst containing 1/2 percent Na_2CO_3 exhibits a somewhat higher activity than the corresponding K_2CO_3 catalyst and especially a better stability (experiment 2). On the whole, however, it differs little from that containing 1/4 percent of Na_2CO_3. At an Na_2CO_3 content of 1 percent, the activity decreases, and especially the life of the catalyst drops considerably (experiment 3). This is even more pronounced when 2 percent Na_2CO_3 is added (experiment 4). In general the following may be said about the influence of an Na_2CO_3 addition: Catalysts containing 1/4 to 1/2 percent K_2CO_3 or Na_2CO_3 work about equally well. However, for reasons given earlier, promotion with K_2CO_3 is to be preferred.

Influence of Copper Content

The catalysts so far discussed contained 20 percent of copper (referred to the iron metal) in all cases. After we had discovered that larger quantities of copper (as, for example, 30 percent) did not improve the activity any further, we investigated copper-deficient iron catalysts. Table 57 shows the results of experiments during which an iron catalyst was used, containing only 5 percent copper. All other conditions, however, remained the same as for the above-mentioned catalysts. The subsequent quantity of K_2CO_3 added amounted to 0, 1/8, 1/4, and 1/2 percent.

Table 57.—Influence of K_2CO_3 upon 20Fe-1Cu catalyst (5 percent Cu)

Experiment No.	K_2CO_3 content, percent	Yield, grams per cubic meter of mixed gas, in days 7	14	21	28	35	42
1	0	29	38	40	44	40	40
2	1/8	53	52	50	50	47	42
3	1/4	56	52	49	47	41	35
4	1/2	50	45	39	—	—	—

The catalyst, which was free of K_2CO_3 (experiment 1), gave a maximum yield of 44 grams after 28 days of operation. Comparison with table 81 (experiment 1) shows that it surpassed the corresponding catalyst containing (Table 87) 20 percent of copper. The catalysts used in experiments 2 and 3/containing 1/8 and 1/4 percent, respectively, of K_2CO_3 had an activity approximately equal to that of the catalyst containing 20 percent of copper. The decrease of activity for the catalyst containing 1/2 percent of K_2CO_3 (experiment 4) is of the same order of magnitude as that of the iron catalysts containing 20 percent of copper.

It should be noted here, however, that by repeating this series of experiments with another catalyst of the same composition, the results could not be duplicated. The maximum yield with the K_2CO_3-free catalyst was only 35 grams, whereas with a catalyst containing 1/4 percent K_2CO_3, only 50 grams were obtained. We found that the catalysts containing 20 percent of copper could be reproduced more easily than those containing smaller amounts.

IRON-COPPER THREE-COMPONENT CATALYSTS PREPARED FROM FERRIC COMPOUNDS

At the same time that we investigated the iron-copper catalysts prepared from ferrous salts, we also carried out experiments on three-component catalysts. The third component was a difficultly reducible oxide, preferably manganese oxide. Earlier, we found that the addition of such an oxide to cobalt and nickel catalysts caused considerable improvement. This led us to investigate whether such an addition to iron catalysts would result in an improvement similar to that of cobalt catalysts. The most prominent metal investigated as a third component was manganese.

It should be noted that the specific action of manganese oxide is not known at present. It appears that the presence of such an oxide in iron-copper catalysts would not be required so far as improvement in yield and regeneration are concerned, but it seems that the presence of such an oxide has a favorable effect upon the life of the catalyst. Obviously all those factors are also a function of the mode of preparation of the catalyst and the choice of operating conditions.

Fe-Cu-MnO Catalysts. Fe-Cu-MnO Normal Catalysts (4:1:1)

The so-called normal catalyst was used to study the influence of the various conditions of preparation, alkali addition, etc. It contained iron metal, copper metal, and presumably MnO (manganese oxide) in the ratio of 4:1:1.

Thermal Decomposition of Nitrates

We investigated catalysts which were prepared by decomposing the nitrates at 250° to 300°C. in a porcelain dish. Heating was continued until all of the nitrous oxides had been dispelled. These decomposition catalysts were inferior to the precipitated catalysts investigated later. The decomposition catalysts were investigated at temperatures ranging between 235° and 250°C. In all cases, the addition of approximately 0.2 to 0.3 or 5 percent of K_2CO_3 to the catalyst was advantageous. The alkali was added in one case to the nitrates as such and in another case to the finished catalyst after thermal decomposition. We could not observe any differences due to adding the alkali in one way or the other. The catalysts free of alkali were less active. The apparent density of the catalysts varied between 1.4 and 1.6. Consequently, it was much higher than that of the later NaOH-precipitated catalyst, which had apparent densities varying between 0.92 and 1.17.

For a catalyst charge containing 4 grams of iron as metal and a gas rate of 4 liters per hour, the decomposition catalysts gave contractions of 25 to 30 percent for 20 to 25 hours when operated at 240° to 250°C. The maximum yield of liquid products recorded was 42 grams per cubic meter. The life of the catalyst was short on account of the high reaction temperature of 250°C. During the first 20 to 40 hours, the contraction decreased by 5 percent; and at the same time, the oil and paraffins formed became yellow. The life of the decomposition catalysts was higher at 235°C.; however, here also, the contractions decreased after 80 to 100 hours of operation. The products started to become yellow after 150 to 200 hours of running. When the decomposition catalysts were used at 235°C., they required 30 to 40 hours of operation before they gave a maximum of 25 percent contraction. The yields amounted to around 30 to 35 grams per cubic meter. A more rapid increase in contraction could be obtained when the catalysts were initially taken into operation at 250°C., and then after the contraction had reached 25 to 30 percent, the temperature could be lowered again to 235°C.

With the decomposition catalysts under normal circumstances we did not observe water formation, but only when the average gas velocity was reduced to 2 or 1 liter per hour. In this case we found some water in the receiver in addition to all the paraffin-rich oil. The ratio of liquid products to water was then approximately 3:1. An increase in yield of liquid products was not connected in any way with the water formation. We shall report on this more in detail in the section on "Experiments on Water Formation".

The product gas of the decomposition catalysts contained a high percentage of CO_2 and H_2 (just as in the case of the precipitated catalyst to be described later). An end gas, obtained at 240°C. and 4 liters per hour and a contraction of 25 percent, had the following composition: CO_2, 18.4; olefins, 1.4; O_2, 0.3; CO, 8.3; H_2, 59.1; hydrocarbons, 3.7; carbon number, 1.51; N_2, 8.8.

The decomposition catalysts could be regenerated with air at a temperature of 220°-250°C., with or without previous extraction of the paraffin. It is to be noted that the regenerated catalysts usually caused the contraction to increase at a slower rate than a freshly prepared catalyst. When the alkali-free decomposition catalysts were repeatedly treated with air, it was observed that the activity of these catalysts slowly increased more and more after each regeneration.

Precipitation with Alkalies

When we resorted to preparing the Fe-Cu-MnO catalyst by precipitation with alkalies, we could notice essential progress as compared to the previously described decomposition catalysts. At first we used alkali bases; later we used alkali carbonates.

Precipitation with NaOH.--A solution of the nitrates in approximately its tenfold weight of water (referred to the Fe-Cu-MnO quantities in the nitrates) was precipitated in portions with a hot solution of NaOH with stirring. The NaOH solution was prepared by dissolving the theoretical quantity of NaOH + 5 percent excess in four times its weight of water. The filtered precipitate was washed four times with the same amount of water as the original liquid. Although such a catalyst still contains some residual alkali as could be detected by analysis, it was necessary, nevertheless, to add some additional alkali in order to obtain an active catalyst. The alkali (a dilute K_2CO_3 solution) was added to the washed catalyst. Then the catalyst was dried at 105°C. and used for the reaction. When NaOH was used as a precipitant, the most favorable quantity of K_2CO_3 was between 0.5 and 1 percent K_2CO_3, referred to the total catalyst. If a larger alkali quantity was used, such as, for instance, 5 percent, the catalyst reached its maximum performance sooner, but it had a shorter life, apparently because increased alkali content favors the formation of high-molecular-weight hydrocarbons, which decompose and cause decomposition products to be left behind on the catalyst. When catalysts were used containing a higher amount of alkali, a greater quantity of solid paraffins at the end of the reaction tube and in the receiver was soon apparent.

The following experiment also shows that with the catalyst containing large amounts of alkali larger quantities of paraffin are retained than in the case of a catalyst carrying the normal alkali content. A catalyst quantity was used which contained 20 grams of iron, 5 grams of copper, and 5 grams of manganese oxide and in addition in one case 1 percent K_2CO_3 and in another 2.5 percent K_2CO_3 After 360 hours of operation (at 220° to 230°C. and 2 liters per hour of gas), extraction of the catalyst with benzene yielded 9.3 grams of paraffin from the catalyst containing 1 percent K_2CO_3 and 17.1 grams of paraffin from the catalyst containing 2.5 percent K_2CO_3. The catalyst containing larger quantities of alkali contained almost twice as much paraffin. This observation is supplemented by the further fact that the catalyst richer in alkali gave only 29 grams of liquid hydrocarbons per cubic meter of gas as compared to 40 grams for the catalyst containing 1 percent K_2CO_3. (In both cases, the temperature was 220°C., and the contraction approximately 28 percent.) On account of the higher boiling points, obviously a greater percentage of the reaction products remained in the more highly alkalized catalyst. A final calculation and addition of all products formed showed that in both cases approximately the same quantity of synthetic products was formed. For the catalyst containing 1 percent K_2CO_3, this total quantity amounted to 49.9 grams, and for the catalyst containing 2.5 percent K_2CO_3, the total yield was 51.5 grams per cubic meter.

In contrast to the decomposition catalysts, the NaOH-precipitated catalysts can be taken into operation at as low a temperature as 235°C., in some cases even at 225° to 230°C., and when large quantities of catalyst are used (such as, for instance, 30 grams), the initial temperature may be as low as 220°C. When a quantity of catalyst corresponding to 10 grams of iron, 2.5 grams of copper, and 2.5 grams of MnO (plus 1 percent K_2CO_3) was used, with a gas rate of 4 liters per hour, the NaOH-precipitated catalysts gave a maximum contraction of 30 to 35 percent after approximately 25 to 30 hours of operation at 235°C. At this point they gave a maximum yield of 45 to 50 grams of liquid product per cubic meter.

We did not carry out any systematic experiments on the life of the NaOH-precipitated catalysts. In general, however, it may be said that they are more stable than the decomposition catalysts on account of the lower reaction temperature (235°C.). However, they are less durable than the soda-precipitated catalysts. For example, we found that an NaOH-precipitated catalyst working at 220° to 230°C. at the end of 360 hours gave 4 percent less contraction than at the beginning of the operation.

The conversion of the mixed gas proceeded in fundamentally the same manner whether an NaOH-precipitated catalyst or a decomposition catalyst was used. Primarily CO_2 was formed, and little water. Detailed data on the relationship between yield, CO_2, and water formation for the NaOH-precipitated catalysts are summarized in the section on "Experiments on Water Formation", tables 66 and 67. When the precipitation of the NaOH catalysts was carried out in the cold and subsequently washed with hot water, a catalyst was obtained which gave a higher contraction more rapidly; however, the contraction fell off after 50 to 60 hours of operation. In addition, the reaction products were yellow despite the fact that the temperature was only 220°C. This phenomenon is ordinarily observed to occur between 240° and 250°C. when using a catalyst which was precipitated hot. The large quantity of residual alkali remaining in the catalyst after precipitating cold is obviously the cause for the initial accelerated activity. Nevertheless, the catalyst was not very durable.

A similar observation was made when the constituents of the Fe-Cu-MnO catalyst were precipitated separately with NaOH from hot solution. The washed slurries were then mixed with mortar and pestle, and 1 percent K_2CO_3 was added. The catalyst thus produced showed an increased activity at 235°C., but the activity reduced rapidly with a consequent formation of yellow reaction products similar to those described above. We demonstrated that by washing each constituent intensively, a catalyst of normal character was produced. It appears that with separate precipitation, larger residual quantities of alkali remain in the catalyst than when the constituents are precipitated simultaneously.

In order to further investigate the influence of residual alkali content upon the activity and the life of the catalyst, the following experiment was carried out: A quantity of catalyst which contained 40 grams of iron and was prepared by precipitating the various constituents separately was divided into four catalyst tubes. Sample 1 was used immediately without further alkali addition. Sample 2 was alkalized with 1 percent K_2CO_3. Samples 3 and 4 were first extracted with water for 24 hours in the Soxhlet apparatus to remove any residual salts originating from the precipitation. After this, sample 3 was immediately taken into operation, but 1 percent K_2CO_3 was added to sample 4 before it was taken into operation.

In the temperature range for which we investigated these conditions, we obtained a comparatively significant picture on the action of the residual alkali and the subsequent alkali addition. Sample 1 (without alkalization) reached a maximum contraction of 26 percent and remained there for 180 hours. Sample 2 (with addition of alkali) reached a maximum of 32 percent contraction very soon, but after 116 hours yielded yellow reaction products. After 188 hours the contraction had decreased to 20 percent. Sample 3 (extracted with water, without alkali addition) gave a contraction of 17 percent and was very active. However, it retained this activity throughout the experiment. Sample 4 (water extracted, with alkali addition) proved to be best. It gave a contraction of 28 percent which is somewhat less than sample 2, but it was essentially more stable, and after 188 hours still caused a contraction of 27 percent. Thus, the catalyst prepared by separate precipitation, obviously on account of its comparatively high residual alkali content, was quite active, even without the addition of extra alkali. It was rather stable, too. By adding additional alkali, its activity was increased but its life considerably suppressed. When the catalyst prepared by separate precipitation was water-extracted, it lost activity, obviously a result of the more efficient removal of residual alkali, when each constituent was washed separately. When this water-extracted catalyst was alkalized in the ordinary manner, a comparatively good and stable catalyst resulted. According to these data, good NaOH-precipitated catalyst should be obtained in the following way: 1, by separate precipitation; 2, by thorough washing and extraction; and 3, by subsequent alkalization.

KOH: We did not find it advantageous to use KOH instead of NaOH as a precipitating agent. The KOH-precipitated catalyst seemed to be comparatively active without additional alkali. The reason for this may be that the residual potassium in the precipitated catalyst acts as a stronger base than the NaOH, and consequently has a greater activating influence. When more alkali was added in the form of potassium carbonate, no essential improvement in activity resulted.

NH_3: NH_3 may be used also for precipitating the iron-copper-manganese catalyst. Precipitation with ammonia is a little more difficult because precipitation of the manganese tends to be incomplete, and formation of the soluble copper complex salt occurs. This difficulty can be prevented by precipitating the three constituents separately, and after washing them carefully, mixing them together in a moist state. Without the addition of alkali the ammonia catalyst was only moderately active; with 1 percent K_2CO_3 it acquired the activity of the NaOH catalyst.

Precipitation with Na_2CO_3 —The sodium carbonate-precipitated catalysts were prepared like the NaOH catalysts, Fe-, Cu-, and Mn-nitrates were dissolved in ten times their weight of water (referred to iron, copper, and manganese oxide content) and precipitated hot with a hot solution of Na_2CO_3 (the solution contained 5 percent excess over the theoretical amount of Na_2CO_3). The soda solution contained 1 part by weight of anhydrous soda to 5 parts by weight of water. The precipitate was washed five times with hot water, each portion being equal to the volume of the original solution, then the still moist precipitate was treated with a required quantity of K_2CO_3; it was dried on the water bath, and finally in the oven at 105°C.

The Fe-Cu-MnO catalysts precipitated with soda showed approximately the same behavior as those precipitated with NaOH; that is, they gave approximately the same average yields of liquid products. Furthermore, the CO conversion took place chiefly with CO_2 formation. As an example, in Table 53, a soda-precipitated Fe-Cu-MnO catalyst containing 0.1 percent K_2CO_3 is described (Fe:Cu:MnO = 10:2.5:2.5). (The added K_2CO_3 quantity is referred to the Fe-Cu-MnO quantity.)

Table 58 shows that the catalyst after 168 hours of operation still gave a somewhat higher conversion than it did after 46 hours. The yield of liquid products amounted to 53 grams per cubic meter. The conversion ratio between CO and H_2 is approximately the same as those of the section on "Experiments on Water Formation", described for the NaOH catalysts. The CO portion used up during the synthesis amounts to 1.2 to 1.3 times that portion which went into CO_2. Seventy-six to eighty-one percent of the CO-oxygen went to CO_2, and only 8 to 12 percent went into water. This is brought out clearly by the end-gas analysis after 168 hours of operation.

Table 58.—Conversion (mixed gas) with Fe-Cu-MnO (10:2.5:2.5) precipitated with sodium carbonate contains 0.1 percent K_2CO_3

Temperature, °C.	235	235
Space velocity, liters per hour	4.3	4.4
Contraction, percent	28.2	32.4
Hours of operation	46	168
CO conversion, percent going to CO_2	40.6	38.2
Unreacted CO	10.5	11.7
Synthesis (difference)	48.9	50.1
CO_2:synthesis	1:1.2	1:1.3
Oxygen conversion:		
percent going to CO_2	81.2	76.4
percent going to H_2O (difference)	8.3	11.9
H_2O:CO_2	1:9.8	1:6.4
Liquid products, grams/cubic meter	Not determined	52

	CO_2	Olefins	O_2	CO	H_2	Hydrocarbons	Carbon No.	N_2
Percent	17.9	1.3	0.1	5.0	59.5	4.8	1.32	11.4

The soda-precipitated catalysts could be taken into operation at 235°C., and by using a gas rate of 4 liters per hour per 10 grams of iron, the maximum contraction was 30 to 34 percent after approximately 25 to 40 hours. This corresponds to a maximum yield of 50 grams per cubic meter of liquid products. Just as in the case of NaOH-precipitated catalysts, here, too, the addition of alkali was required. We found that 0.1 to 0.2 percent K_2CO_3 was sufficient. When a larger quantity of K_2CO_3 was added (up to 2 percent) the catalyst had an initially higher activity which could be recognized in the more rapid increase in contraction. However, the life of the catalyst decreased. With higher alkali content, the formation of the yellow reaction products set in earlier and was soon followed by decrease of catalyst activity.

The soda-precipitated Fe-Cu-MnO catalyst seemed more sensitive than the corresponding NaOH catalyst. At a temperature of 245° to 250°C., the catalyst quickly began to lose activity.

Extended experiments devoted to investigation of the durability and reactivation of the sodium carbonate-precipitated catalyst were not carried out. Over a period of 200 hours these catalysts proved more durable than the sodium hydroxide-precipitated catalysts. With respect to water formation, the soda catalyst behaved in the same manner as the NaOH catalyst did at higher temperature or at lower gas rates.

K_2CO_3: Only very meager experimental results are available on the use of potassium carbonate as a precipitating agent. The results show that a catalyst precipitated by K_2CO_3 can give a contraction of 24 percent (4 liters per hour at 230°C.), even without subsequent addition of alkali. Similar results have been reported for the KOH catalysts. Since further addition of K_2CO_3 to the catalyst precipitated with K_2CO_3 probably would not cause the activity to increase any further, we investigated the influence which Na_2CO_3, Rb_2CO_3, and potassium acetate (each 1 percent) had as a promoter. We observed that the weaker base (Na_2CO_3) had no influence; nor did potassium acetate have any influence. However, no damaging effects resulted from their addition. The addition of Rb_2CO_3 caused the early appearance of yellow reaction products. The contraction was not increased by the addition of Rb.

$(NH_4)_2CO_3$:

We investigated more in detail the Fe-Cu-MnO catalyst which was precipitated with ammonium carbonate. Ammonium carbonate has the same effect as ammonia. To avoid incomplete precipitation or the formation of the water-soluble complex salt, it is recommended to carry out the precipitation of the various components separately and then to mix them in a moist state.

The behavior of the catalysts precipitated with ammonium carbonate but not impregnated with alkali is described in greater detail in the section on "Experiments on Water Formation" in connection with the question of whether a relationship exists between the CO_2 formation of the iron catalyst and its alkali content.

The Fe-Cu-MnO catalysts not treated with alkali had little activity and resembled those obtained by precipitation with ammonia. In order to activate them, they had to be treated with K_2CO_3, and like the Na_2CO_3 catalysts, 0.1 to 0.2 percent had to be added. We found that this quantity was also sufficient for the catalysts precipitated with ammonium carbonate. In this manner, we succeeded in preparing a catalyst which gave a contraction of 28 percent with 4 liters of gas per hour at 230°C., and at 235°C. the contraction was 32 percent. However, it seems that the ammonium carbonate catalyst is not superior to the soda catalyst.

Variation of Copper and Manganese Content in Fe-Cu-MnO Catalysts

In the previous experiments, the catalyst contained Fe-Cu- and MnO in the ratios of 4:1:1. Qualitative experiments in which the copper and manganese proportions were varied were carried out. The percentage contraction was the measure of catalyst activity. We found that the ratio of copper and manganese to iron may be changed within wide limits without causing marked changes in catalyst performance. For this series of experiments, we used NaOH-precipitated catalysts which had been treated with 0.5 percent K_2CO_3. The quantity of catalyst was chosen to provide 8 grams of iron. (It is obvious that, on account of this restriction, the total quantity of catalyst was different for the various experiments as the copper and manganese content changed.) We worked at an experimental temperature of 250°C. in order to study the stability and life of the catalyst more rapidly. We used the following:

1. 14 grams Fe-Cu-MnO in the ratio of 4:1:1
2. 18 grams Fe-Cu-MnO in the ratio of 4:1:4
3. 24 grams Fe-Cu-MnO in the ratio of 4:4:4
4. 13 grams Fe-Cu-MnO in the ratio of 4:0.5:1

The experiment shows that, with 4 liters per hour and 250°C., the catalyst gave the following maximum contraction:

	Catalyst			
	1	2	3	4
Percent	25	26	25	20

The contraction decreased to 80 percent of the maximum contraction after 420, 450, 420, and 440 hours, respectively.

With the exception of the somewhat weaker catalyst 4, all catalysts behaved very similarly. On the scale of the present experiment, it made little difference whether the iron content of the catalyst varied between 33 and 62 percent, the copper content between 7.7 and 33 percent, or the manganese oxide content between 29 and 44 percent. It should be mentioned that catalyst 1 gave 42 grams of liquid products per cubic meter after 447 hours of operation, whereas catalyst 3 gave only 37 grams of liquid products per cubic meter.

A further series of experiments showed that the copper and manganese content of the catalyst may be reduced to a very low percentage; and as the section on "Copper-Free Iron Catalysts" reports, if these constituents are missing entirely the experimental conditions must be adjusted accordingly and longer induction periods are usually necessary before such a catalyst reaches its maximum performance.

In the following, two copper- and manganese oxide-deficient catalysts are mentioned, having composition (1) Fe:Cu:MnO = 10:0.2:0.2 and (2) 10:0.1:0.1. Both catalysts were alkalized with 0.2 percent K_2CO_3. The catalyst which was precipitated with soda behaved most favorably. At 235°C. and 4 liters of gas per hour, it reached the maximum contraction of 26 percent, which it also maintained when the temperature was lowered to 230°C. The yield of liquid products at 230°C. was 40 grams per cubic meter. The catalyst was operated for a short time at 225°C. giving a 22-percent contraction. When the temperature was raised again to 230°C., the catalyst continued to give a contraction of 24 percent for another 298 hours. The catalyst which was precipitated with ammonium carbonate Fe-Cu-MnO = 10:0.2:0.2, performed more slowly. It gave the following contractions at 235°C. and 4 liters of gas per hour:

Hours	1	53	118	191	239	286
Contraction, percent	5	14	20	21	22	23

After the 118th hour of operation, the contraction increased only very little; but after 12 days of operation, a maximum contraction apparently had not yet been reached.

Although the experiment described here has no practical significance, it demonstrates the interesting fact that it is possible to activate slowly the apparently inactive copper-manganese oxide-deficient catalyst. For practical purposes, it appears that one can get by with considerably less copper and manganese than is contained in the so-called normal Fe-Cu-MnO catalyst containing Fe-Cu-MnO in the ratio of 4:1:1.

Significance of Alkali Addition to Fe-Cu-MnO Catalysts

The significance of the addition of alkali for the activation of the Fe-Cu-MnO catalyst has already been discussed in connection with the various modes of catalyst preparation. In the following, the various observations are once more summarized. We have found that catalysts not containing any alkali (as for instance, decomposition catalysts or those precipitated with ammonia or ammonium carbonate) exhibit only little activity. These catalysts require an additional quantity of approximately 0.5 percent alkali, and we believe that K_2CO_3 is the best salt. The situation is not quite as clear in the case of catalysts precipitated with alkali hydroxides or alkali carbonates. In this case, despite the fact that intensive washing is carried out, a certain quantity of residual alkali remains in the catalyst which acts as a promoter and which is capable of producing full catalyst activity. In such a case, the addition of more alkali is not required. The occasional observation that precipitation catalysts exhibit high activity, even without subsequent impregnation (for instance, catalysts precipitated with a stronger base such as K_2CO_3 or catalysts in which the components are precipitated separately), may be explained by the presence of this uncontrollable residual alkali which remains in the catalyst after washing. This quantity of residual alkali can vary considerably. If a further quantity of alkali, such as K_2CO_3, is added to such a catalyst, the extra alkali might not have any beneficial effect; in some cases, the effect is even damaging. To exclude the varying effects resulting from the residual alkali, it is advantageous to wash the precipitate as well as possible with water or to extract with water. After extraction, 0.1 to 0.2 percent K_2CO_3 should be added.

Iron-Copper Catalyst with Zinc, Chromium, Aluminum, and Tin

The question was raised whether manganous oxide may be replaced in the Fe-Cu catalyst by other oxides, such as tin, chromium, aluminum, or zinc. So far, only orienting experiments have been conducted.

Zinc.—A catalyst which was precipitated by soda and contained Fe-Cu-ZnO in the ratio 10:2.5:2.5 in addition to 0.2 percent K_2CO_3 corresponded in activity to a manganese catalyst. The catalyst gave 27 percent contraction at 225°C. at a gas rate of 4 liters per hour. After the temperature reached 235°C., the contraction increased to 31 percent. Without the addition of alkali, a contraction of 23 percent at 235°C. could not be surpassed.

Chromium.—In an older series of experiments with chromium, two NaOH-precipitated catalysts containing different amounts of chromium were investigated; namely:

1. $Fe-Cu-Cr_2O_3$ 8:2:2 + 0.5 percent K_2CO_3
2. $Fe-Cu-Cr_2O_3$ 8:2:8 + 0.5 percent K_2CO_3

Catalyst 2 was practically inactive and at 240°C. gave only 8 percent contraction. Catalyst 1 gave 18-percent contraction at 240°C. and 28 percent at 250°C. After oxidation with air at 250°C. neither of the catalysts could be used any longer, nor did treatment with H_2 at 400°C. to reduce any chromate yield any better results. The corresponding decomposition products, having compositions 1 and 2, were even less active than the precipitated catalysts.

Aluminum.—By precipitation with soda from the nitrates, a $Fe-Cu-Al_2O_3$ was prepared. This catalyst gave a maximum contraction of 25 percent and lost its activity very rapidly. When the catalyst was impregnated with 1 percent K_2CO_3, the contraction was only 17 percent at 235°C.

Tin.—Two catalysts containing tin were prepared by decomposition of the nitrates. The required tin was added to the mixture of the nitrates as SnO_2, calculated as metastannic acid (from tin, nitric acid). The catalyst was almost entirely inactive; in both cases only small amounts of oil formed. No contraction was observed at 250°C. The catalyst had the following composition: $Fe-SnO_2-MnO$ = 4:1:1 + 0.5 percent K_2CO_3. The other catalyst had the composition, $Fe-Cu-SnO_2$ = 4:1:1 containing 0.5 percent K_2CO_3 also.

Appendix—Catalysts of Special Composition

In addition to the Fe three-component catalysts, we desire to describe a few more experiments in which catalysts of a special composition or preparation were investigated.

Iron-Manganese.—The following experiments show that iron-manganese catalysts which do not contain copper exhibit some activity at 235°C. A catalyst which was precipitated with soda and consisted of Fe and MnO in the ratio of 10:2.5 plus 0.5 percent K_2CO_3 gave 12-percent contraction after 24 hours and 20-percent contraction after 42 hours, and a maximum contraction of 23 percent after 69 hours (space velocity, 4 liters per hour of mixed gas). After 69 hours, the reaction products became yellowish and after 114 hours, the contraction started to decrease.

When the same catalyst was used, however, without the alkali, the time of induction was considerably longer. A contraction of only 11 percent was reached after 69 hours, and 18 percent after 162 hours. After 210 hours, the contraction was 20 percent, the maximum contraction at 235°C. When the temperature was raised to 240°C., the contraction increased to 25 percent (after approximately 282 hours). A previous reduction with H_2 at 350° to 450°C. (1-1/2 to 2 hours of treatment) was of no influence on either the alkali-free or the alkalized catalyst. Further details on the copper-free iron catalyst are discussed in the section on "Copper-Free Iron Catalysts".

Iron-Magnesium.—A catalyst reduced by thermal decomposition of Fe nitrate and a solution of MgO in nitric acid contains the two metals Fe and MgO in the ratio of 1:1. This catalyst was used at 260°C. with mixed gas, and no contraction could be observed. When 0.75 percent K_2CO_3 was added and an H_2 treatment at 350°C. was performed, no better results were observed.

Iron Salts.—By precipitating ferric nitrate or ferrous chloride with disodium phosphate, the voluminous iron phosphate was obtained. At temperatures up to 260°C. with mixed gas, the phosphate catalyst gave no contraction. Oxidation at 250°C. and H_2 reduction at 300° to 350°C. had no effect. An iron borate-precipitated catalyst, which was obtained by allowing iron hydroxide (from ferric nitrate with ammonia) to react with a boric acid solution, was just as ineffective. At reaction temperatures, considerable quantities of boric acid were removed by sublimation. Another borate which we produced by treating ferric nitrate solution with borax was not effective. The unwashed preparation yielded nitric acid, nitrous oxides, and water for a long time when heated in a stream of mixed gas. Boric acid was lost by sublimation.

Iron (2) carbonate.—For the preparation of ferrous carbonate, we mixed lead nitrate with the calculated quantity of ferrous sulfate in a dry state and added a few drops of sodium hydroxide solution. Then the mixture was digested in a solution containing 250 cc. of water and 250 cc. of alcohol until all the ferrous sulfate was converted. The solution containing a precipitate of lead sulfate was filtered; the light-green clear filtrate containing ferrous nitrate was heated and precipitated with a hot sodium bicarbonate solution in an atmosphere of nitrogen. The filtration and washing operation of the grayish-white ferrous carbonate precipitate was also carried out in a nitrogen atmosphere. Nevertheless, a superficial discoloration (oxidation) of the carbonate occurred. When the carbonate was allowed to act on mixed gas, a contraction could only be observed above 240°C. The maximum contraction of 19 percent was observed at 250°C. After 8 hours of operation the products assumed a yellow discoloration, and activity decreased.

NEEDLE-IRON-ORE CATALYSTS (Meyer)

According to Fricke and Ackermann (37), during the dehydration of synthetic needle iron ore (alpha $Fe_2O_3 \cdot 1H_2O$) the lower the dehydration temperature the more active the alpha iron III oxide obtained. The internal energy differences amounted to up to 5 kilogram-calories per mole of Fe_2O_3. The oxides which were high in energy upon X-ray analysis showed a more random crystalline structure. Since the scattered crystal structure is responsible for the catalytic behavior of the oxides, it appeared interesting to us to investigate the catalytic activity of the needle iron ore with respect to the $CO-H_2$ reaction.

Preparation of Synthetic Needle Iron Ore (alpha $Fe_2O_3 \cdot 1H_2O$)

In the preparation of the needle iron ore, we used the method of Fricke and Ackermann.

A solution containing 1 mole of iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) in 1 liter of water was added, under violent agitation, to a solution containing 3-1/2 moles of ammonia per liter of water. The precipitate of oxyhydrate was washed seven times, each time with 4 liters of water. The separation of wash water from the precipitate was accomplished by decantation and subsequent filtration. All operations were carried out in the cold. Before being dried, the moist, amorphous mass of oxyhydrate was mixed with twice its quantity of concentrated KOH solution. Then the mixture was heated for 2 hours to 140° to 160°C. in a silver-lined autoclave. The reaction product, which was bright yellow, was filtered off and washed with water six times.

Results of Experiments

At first, the catalytic behavior of the needle iron ore was compared with that of other iron catalysts. We compared its activity with an iron catalyst which was precipitated from iron nitrate with soda. This catalyst, after careful washing, was digested at room temperature with 2-normal KOH solution. After this digestion, it was washed again in the usual manner. The catalyst thus contained approximately the same quantity of KOH after the washing operation as did the needle iron ore catalyst. Both catalysts were dehydrated in a current of air at 210°C. (2 hours); then they were treated with H_2 for 4 hours at 210°C. and taken into operation with mixed gas (4 liters per hour). When the activity of the needle iron ore was compared with the activity of the other iron catalysts, it was observed that it displayed about twice the activity of the ordinary catalysts. At 240°C. the needle-iron-ore catalyst gave a contraction of 8.5 percent, whereas the contraction of the other catalysts was only 4.5 percent. When the gas velocity was reduced to 1 liter per hour, the needle-iron-ore catalyst gave a contraction of 29 percent and a yield of liquid hydrocarbons of 25 grams per cubic meter of mixed gas. The other catalyst gave, under the same conditions, only 10 grams of liquid products. The activity of the needle iron ore was of the same order of magnitude when the catalyst was used for the synthesis with mixed gas directly without previous dehydration. A dehydration of the catalyst at ordinary pressure or in a vacuum over phosphorus pentoxide had apparently no effect upon the activity.

The preparation of needle iron ore does not proceed in the presence of copper. Therefore, we have mixed the finished needle iron ore in a moist state with freshly prepared copper carbonate (obtained by precipitating copper nitrate solution with potassium carbonate) and added 25 percent of copper based on the iron. With this copper-containing needle-iron-ore catalyst (4 grams of iron) and a flow velocity of 4 liters per hour, a maximum contraction of 25 percent was observed, yielding 40 grams of liquid products per cubic meter of mixed gas. The life of the catalyst was short, however. If the copper addition is carried out by mixing the components together in a dry state, the needle iron ore is not activated to as high an extent.

Furthermore, we discovered that kieselguhr added to the copper-containing needle iron ore (added to the moist paste) caused the activity to decrease. In the same way, the activity decreased when 1/2 percent K_2CO_3 was added after the copper addition. As the life of the needle-iron-ore catalyst was comparatively short when 4 grams of iron were used with a gas velocity of 4 liters per hour, the catalyst quantity was increased from 4 grams to 10 grams of iron, at the same gas velocity, since the bulk density of the needle-iron-ore catalyst as compared to cobalt and nickel catalysts is approximately four times greater. The following experiments, therefore, refer always to 10 grams of iron, a catalyst layer length of 30 centimeters, and a flow velocity of 4 liters per hour.

Table 59 gives the results with a copper-free needle iron ore which was dehydrated under various conditions.

Table 59.—Dehydrogenation of needle iron ore with or without copper under various conditions

Experiment No.	Catalyst 10 grams of iron	Pretreatment	Temperature, °C.	Maximum contraction, percent	Yield, grams per cubic meter of mixed gas
1	Needle iron ore	Mixed gas immediately	233	13	12
2	Needle iron ore	2-hour air, 210°C., then mixed gas	233	13	13
3	Needle iron ore	16-hour air, 210°C., 1-hour air, 400°C.	233	28	41
4	Needle iron ore	16-hour H_2, 210°C., 1-hour H_2, 400°C.	233	2	Almost inactive
5	Needle iron ore + 25 percent copper	Mixed gas immediately	230	31	49-50
6	Needle iron ore + 25 percent copper	2-hour air, 210°C., then mixed gas	233	29	50
7	Needle iron ore + 25 percent copper	16-hour air, 210°C., 1-hour air, 400°C.	233	28	47
8	Needle iron ore + 25 percent copper	16-hour H_2, 210°C., 1-hour H_2, 400°C.	233	26	40
9	$CuCO_3$ added after treatment with air at 400°C.	16-hour air, 210°C., 1-hour air, 400°C.	242	21	26

As already mentioned with regard to activity, it did not matter whether the needle iron ore was dehydrated at first for 2 hours in the presence of air at 210°C. or whether the catalyst was taken into operation with mixed gas immediately (experiments 1 and 2). Previous to experiment 3, the needle iron ore was dehydrated in a stream of air for 16 hours at 400°C. By doing this, the activity was increased considerably, and the yield improved from 13 to 41 grams per cubic meter of mixed gas. However, the results of this experiment were difficult to reproduce. When the dehydration was carried out in the presence of hydrogen instead of air again at 400°C., the needle iron ore acquired only a very slight activity (experiment 4).

For experiments 5 to 8, a needle iron ore was used that contained 25 percent of copper as carbonate. The mode of mixing the copper into the moist catalyst was described earlier. A maximum yield of 50 grams of liquid products (experiments 5 and 6) was obtained, irrespective of whether the catalyst was taken into operation immediately with mixed gas or whether it was dehydrated first in a stream of air at 210°C. In contrast to the copper-free needle iron ore, the dehydration of the copper-containing catalysts in a stream of air at 400°C. did not cause an increase of activity (experiment 7). Dehydration in a stream of H_2 at 400°C. led to a somewhat smaller activity (experiment 8). Finally, we investigated the activity of a catalyst in which the copper was added in the dry state after dehydration of the needle iron ore in a stream of air at 400°C. This catalyst showed an activity 50 percent below that of the moist catalyst (experiment 9).

We further investigated the activity of a copper-containing needle-iron-ore catalyst in which Fe and Cu were present in the same ratio as the previous needle-iron-ore copper catalysts, but in which the alpha $Fe_2O_3 \cdot 1H_2O$ component was amorphous Fe_2O_3 instead of crystalline Fe_2O_3. The amorphous iron oxide obtained by precipitation with ammonia after washing with water was divided in half. The first half was converted into needle iron ore by applying heat under pressure at a temperature of 150°C. in the presence of KOH, and thereafter the catalyst was mixed with copper carbonate. The other half was mixed with the corresponding quantity of KOH at room temperature and was then mixed with copper carbonate. Both catalysts were taken into operation with mixed gas without pretreatment. They furnished the results indicated in table 60. The needle-iron-ore catalyst containing the crystallized iron oxide is far superior in activity to the catalyst containing amorphous iron oxide. It was found that the yields for the crystalline catalyst were approximately three to four times as high as those of the amorphous catalyst. This increased activity may be easily explained by a change of the crystalline structure which takes place within the needle iron ore after dehydration. During dehydration, the water held in the crystalline structure of the catalyst is either totally or partly removed; and by doing so, a random crystalline structure is produced.

With reference to the life of the catalyst, one observes from table 60, experiment 2, that the maximum yield was obtained after approximately 12 days; however, after 22 days, only 41 grams of liquid products were produced. When twice the catalyst quantity was used (20 grams of iron), the activity remained unchanged during 22 days, whereas after 42 days only 37 grams of liquid products were formed.

The increase in activity which resulted from the addition of copper to the needle iron ore was not further improved by the addition of thorium for instance, or Mn. In table 61 the results are described with needle-iron-ore catalysts which, in addition to copper, also contained thorium and Mn. For experiment 1, the moist, copper-containing needle-iron-ore catalyst was mixed with thoria, which was precipitated from thorium nitrate with potassium carbonate. The copper-containing needle-iron-ore catalysts prior to the thoria addition had been dried at 100°C. Catalyst 2 was prepared in such a manner that precipitated copper and thoria were mixed with the needle iron ore in a moist state. For experiment 3, copper-containing needle iron ore was mixed as a moist paste with freshly prepared thoria. The addition of manganese (experiments 4 to 6) was carried out in a similar manner. All catalysts furnished a maximum yield of 49 to 52 grams per cubic meter of mixed gas. The specific influence of the thorium or manganese upon the activity of the catalyst could not therefore be observed. Regarding the life of the catalyst, it may be said that the thoria-containing catalysts are somewhat better than the manganese catalysts.

Simplified Preparation of Needle Iron Ore

In the course of the investigation of the catalytic properties of needle-iron-ore catalysts, we also investigated the possibilities of preparing them in a simpler manner. We want to report on these experiments briefly. To start with, we endeavored to prepare the needle iron ore in the presence of precipitated coppe in order to produce a more homogeneous iron-copper mixture. The preparation of needle iron ore in the presence of copper was not successful. In every instance, we obtained amorphous Fe_2O_3 mixed with CuO, which could easily be recognized from the color of the reaction product. It should be mentioned here that the needle iron ore, in contrast to the amorphous oxyhydrate, is more voluminous, forms larger granules, and is comparatively easier to filter. The product obtained, which was prepared in the presence of copper with KOH under heat and pressure, did not exhibit these properties. Also, when the iron and copper were coprecipitated with potassium carbonate or sodium hydroxide, and when heat and pressure were applied in the presence of potassium hydroxide no needle iron ore was produced. The catalytic activity of these products was slight. The highest contraction was 15 percent at 250°C.

Further experiments were concerned with a simplified method of producing needle iron ore in the absence of copper. Thus, the recommendation by Fricke and Ackermann for an intensive washing operation of the amorphous oxyhydrate precipitated with ammonia seemed superfluous. It was sufficient to wash once with water; the application of heat under pressure with KOH produced the needle iron ore (1 mole of iron was washed with 1 liter of water). Application of heat under pressure and treatment with NaOH instead of KOH did not give any results after previous intensive washing. Furthermore, the use of an autoclave lined with silver seems to be absolutely necessary. When all the other conditions were most carefully observed and when we used an iron- or copper-lined autoclave, no needle iron ore was obtained. It is therefore probable that the silver catalyzes the formation of the needle iron ore.

We found that precipitation of the iron may be carried out with potassium hydroxide or potassium carbonate instead of ammonia. Even with incomplete washing needle iron ore can be obtained by heating under pressure in the presence of KOH. When the usual quantity of copper was added, a yield of 50 grams per cubic meter of mixed gas was obtained.

Table 60.—Influence of KOH, pressure, heat application, and catalyst quantity upon yield and life

Experiment No.	Catalyst, 10 grams of iron	Temperature, °C.	Maximum contraction, percent	Maximum yield, grams per cubic meter of mixed gas	Yield in grams after		
					12	22	42
					days		
1	Fe precipitate with ammonia after KOH treatment at room temperature with $CuCO_3$. No application of heat and pressure.	230	13	14	12	—	—
2	Fe precipitate with ammonia after application of heat and pressure in presence of KOH mixed with $CuCO_3$.	230	30	49	47	41	—
3	Catalyst identical with No. 2, but with 20 grams of iron.	230	31	51	49	48	37

Table 61.—Influence of various additions to copper-containing needle iron ore

Experiment No.	Percent added to the needle iron ore	Mode of addition	Temperature, °C.	Maximum contraction, percent	Grams of liquid products per cubic meter of mixed gas	Remarks
1	25 Cu, 18 ThO_2	Needle iron ore plus Cu (at 100°C. dried) mixed with freshly precipitated thoria.	230	31	52	After 17 days, 43 grams still obtained
2	25 Cu, 18 ThO_2	Cu plus thorium precipitated simultaneously with K_2CO_3 washed and mixed in moist state with needle iron ore.	234	29	51	After 18 days, 41 grams still obtained
3	25 Cu, 18 ThO_2	Precipitated Cu mixed moist with needle iron ore; to this, moist precipitated thoria is added.	235	30	49	After 17 days, 43 grams still obtained

Table 61 (continued)

4	25 Cu, 20 Mn	Needle iron ore plus Cu (at 100°C. dried) mixed with freshly precipitated manganese in moist state.	234	29	50	—
5	25 Cu, 20 Mn	Cu and manganese precipitated simultaneously and mixed with needle iron ore in moist condition.	232	29	51	After 18 days, 35 grams still obtained
6	25 Cu, 20 Mn	Precipitated Cu mixed with needle iron ore in moist condition, then moist precipitated manganese is added.	235	29	49	After 17 days, 33 grams still obtained

By heating commercial Fe_2O_3 under pressure (in the presence of KOH at 160°C.) apparently unchanged Fe_2O_3 was obtained, which at 270°C. was inactive.

The investigation of the catalytic behavior of needle-iron-ore catalysts as used for the gasoline synthesis may be summarized by saying that the needle-iron-ore catalysts exhibit a higher activity than the corresponding iron catalysts prepared in the usual manner, that is, where the iron is present as amorphous Fe_2O_3. The maximum yield obtained with needle-iron-ore catalysts amounted to 53 grams per cubic meter of mixed gas. The use of needle-iron-ore catalysts, however, does not seem practical, since their production requires a great deal of time and is rather complicated. Furthermore, it may be seen from the section on "Iron-Copper Catalysts from Ferrous Compounds" that the ordinary iron catalysts prepared in much simpler ways have higher activities and exhibit longer lifetimes.

INFLUENCE OF PRETREATMENT OF IRON CATALYSTS

Influence of CO Pretreatment (Meyer)

The iron catalysts so far discussed, with or without the addition of K_2CO_3, have been used for the synthesis with mixed gas immediately after they were dried at 105°C. Maximum activity is reached after a certain induction period, which for the alkalized catalysts becomes shorter with increasing alkali content. As already mentioned, the time of induction for a catalyst containing 1/4 to 1/8 percent K_2CO_3 is of 1 to 2 days. With 1/16 percent K_2CO_3 approximately 3 days are required. For catalysts which do not contain excess alkali, the time of induction may be as high as 14 days.

Influence of CO Induction at Synthesis Temperature

We have investigated the effect on activity and on the induction period of a special pretreatment of the catalyst. Experiments 1 to 4 of table 62 were carried out with Fe-Cu-Mn catalysts which were prepared by precipitating $FeCl_2$, $CuCl_2$, and $MnCl_2$ with sodium carbonate. One-half percent K_2CO_3 was used for impregnation.

Catalyst 1 was taken into operation with mixed gas at once. Catalyst 2 was treated first with CO for 24 hours, and catalyst 3 was treated with CO and then H_2 for 24 hours each. Catalyst 4 was treated first with mixed gas and then H_2 for 24 hours each. The pretreatment temperature in all cases was 235°C. The contractions obtained after 25 hours of operation were 5, 17, 28, and 31 percent, respectively. In experiment 4, it should be remembered that the catalyst had already acted upon mixed gas for 24 hours before the H_2 treatment was performed. On the whole, for all experiments, the same maximum activity was observed as regards the yield of liquid hydrocarbons and percentage contraction. With respect to the stability of the catalysts, no worthwhile differences could be observed, for in all cases the average yield was the same after 17 days of operation (last column, table 62). The life of these catalysts was not too satisfactory, probably because they contained 1/2 percent K_2CO_3.

Table 62.—Influence of pretreatment with CO

Experiment No.	Catalyst composition	Pretreatment of catalyst	Temperature, °C.	Contraction after five hours, percent	Maximum contraction, percent	Maximum yield, grams per cubic meter of mixed gas	Average yield after 17 days of operation, grams per cubic meter of mixed gas
1	5Fe-1Cu-1 Mn+1/2% K_2CO_3	Mixed gas immediately	228	5	30	49	47
2	5Fe-1Cu-1 Mn+1/2% K_2CO_3	24-hour CO, then mixed gas	228	17	32	50	47
3	5Fe-1Cu-1 Mn+1/2% K_2CO_3	24-hour CO, 24-hour H_2, then mixed gas	228	18	30	49	45
4	5Fe-1Cu-1 Mn+1/2% K_2CO_3	24-hour mixed gas, 24-hour H_2, then mixed gas	228	31	30	49	44
5	5Fe-1Cu + 1/2% K_2CO_3	Mixed gas immediately	230	After 2-hour 4%	31	55	—
6	5Fe-1Cu + 1/2% K_2CO_3	2-hour mixed gas, 2-hour H_2, then mixed gas	230	After 2-hour 8%	32	52	—
7	5Fe-1Cu + 1/2% K_2CO_3	2-hour CO, 2-hour H_2, then mixed gas	230	After 2-hour 16%	31	53	—

If a previous pretreatment with CO shortens the induction time of the catalyst (as referred to the moment when mixed gas was admitted) the induction time for these experiments cannot be considered shortened, since the pretreatment with CO requires 24 to 48 hours itself.

For further experiments where a manganese-free 5Fe-1Cu catalyst was used which contained 1/2 percent K_2CO_3, the time of pretreatment was reduced from 24 to 2 hours (experiments 5 to 7). When experiments 6 and 7 are compared, one finds that for the run with CO treatment and following H_2 treatment, a contraction of 16 percent was measured even when the catalyst was pretreated for only 2 hours. When pretreatment was carried out with mixed gas and then H_2, the contraction after the same length of time was only 8 percent. The two catalysts, however, do not differ in their maximum activities. In this series of experiments, the catalyst which acted upon mixed gas immediately produced a contraction of 4 percent after 2 hours, and after it had produced its maximum contraction, it was recognized to be somewhat superior to the pretreated catalysts (experiment 5). The experiment indicates that the time of induction of the catalysts when CO is used may be shortened; however, no other advantages, such as, for instance, an increased length of life, resulted.

Influence of CO Pretreatment at Higher-than-Synthesis Temperature (Bahr)

In addition to the previously described experiments, we investigated the influence of a short pretreatment with CO upon induction time when the pretreatment is carried out at a higher temperature than the later reaction temperature.

For these experiments, we used Fe-Cu-MnO catalysts containing these constituents in the ratio 10:2.5:2.5. Five-tenths percent of K_2CO_3 was added. The catalysts were prepared by precipitating ferric nitrate with sodium hydroxide. The investigated range of temperature was between 250° and 270°C. To start with, the catalyst was brought to the experiment temperature in a stream of air; then it was treated with CO for the desired length of time at a flow velocity of 4 liters of CO per hour. Then the temperature was lowered to 230°C. and mixed gas introduced. It should be mentioned here that in the experiments carried out, uniform and reproducible results could not always be obtained. Nevertheless, the following information was obtained.

When the catalyst was taken into operation in the normal way immediately with mixed gas, it gave 5- to 8-percent contraction after 2 hours and 8- to 10-percent contraction after 3 to 4 hours. When the catalyst was pretreated with CO for 1 to 2 hours, a very great reduction in induction time resulted. When the pretreatment was carried out for 1 to 2 hours at 250°C., the catalyst gave 19-percent contraction; after 1 hour at 230°C. and after 3 to 5 hours, it yielded 26-percent contraction. When the CO treatment was carried out at 260°C., a contraction of 17 percent was observed in the following synthesis at 230°C. after 1/4 hour, and 22 percent after 3/4 hour, but after 4 hours, the contraction did not go beyond 25 percent. When the temperature of the CO pretreatment operation was increased to 270°C., no further favorable results were obtained. When mixed gas was admitted to such a catalyst, the contractions were lower than in the case of the catalyst which was pretreated at 260°C. For example, after 15 minutes the contraction was 11 percent, after 3/4 hour 14 percent, and after 2 hours 18 percent. In some cases, we succeeded in producing a catalyst which reached its maximum contraction quickly at 220°C. reaction temperature. This catalyst was pretreated with CO at 250°C. for 2 hours. Thus, for this catalyst, we obtained 9-percent contraction after 1/4 hour, 15 percent after 1/2 hour, and 20 percent after 2 hours.

During the CO treatment at 250° to 270°C., the following observations were made: Immediately after the passage of the CO, the exit gas showed very high concentrations of CO_2 (up to 90 percent). After 1/2 to 3/4 hour the CO_2 content was lower and, depending on the temperature, approached a constant value of 10 to 20 percent. Generally, a contraction was not observed in the beginning. At 250°C., and after 1 to 2 hours, no contraction was observed. At 260° to 270°C., contractions as high as 13 percent occurred. Here, apparently, partial decomposition of the CO occurred with carbon formation.

Not only did the contraction reach a higher value after a shorter time of induction when the catalyst was pretreated, but the visible oil formation was considerably accelerated by the CO treatment. For a catalyst taken into operation with mixed gas under normal conditions, the visible oil formed at 235°C. after 2 to 3 hours. With a pretreated catalyst, however, visible oil formation was observed 1 hour after mixed gas was admitted. In most cases we could observe the formation of oil after 1/4 to 1/2 hour--in some cases, even after 5 to 10 minutes.

We observed that a CO treatment at higher temperatures shortened the time of induction considerably and caused a greater contraction, as compared to a catalyst which was not pretreated. However, it appears that CO pretreatment is not practicable, since we observed that pretreated catalysts in general did not give a higher yield. In some cases, CO pretreatment was detrimental to the yield. Thus we observed that the catalysts described here gave a contraction of 20 to 25 percent in a comparatively short time; however, they reached maximum contractions of 30 to 33 percent only after approximately 30 hours. In several cases the contraction even remained below 30 percent. We also noticed that the pretreated catalysts had a shorter life than the normal catalyst and that they had a tendency to form yellowish products comparatively early, especially when the pretreatment was carried out between 250° and 260°C.

If it should be desired, nevertheless, to carry out a CO pretreatment of the catalyst, it is recommended to pretreat for approximately 1 hour at 240°C. It is perhaps better to use a CO-deficient gas, as, for instance, producer gas, in order to avoid local overheating of the catalyst by a too rapid reduction.

The influence of a CO treatment upon copper-free iron-manganese catalysts was also investigated. The pretreatment, however, had no favorable effect upon the contraction.

Pretreatment with Mixed Gas at Higher Temperatures (Bahr)

We have attempted to shorten the time of induction for the iron catalysts by treating them for a short time with mixed gas at a temperature higher than reaction temperature. The investigated temperature range was 250° to 300°C.; the time of pretreatment was 1 to 2 hours. As an example, the following experiments are described.

An Fe-Cu-MnO catalyst containing the metals in the ratio of 10:2.5:2.5 was heated to 250°C. in a stream of mixed gas for 3/4 hour. Then it was heated for another hour at 250°C. with mixed gas. After this time, it produced a contraction of 14 percent. When the reaction temperature was lowered to 230°C., visible oil formation set in after 5 minutes. The contraction, after 1/4 hour, was 10 percent, after 5 hours, 14 percent, and after 20 hours, 20 percent.

The same catalyst was treated for 2 hours with mixed gas at 260°C. After lowering the reaction temperature to 230°C., the contraction after 15 minutes was 6 percent, and after 4 hours, it was 7 percent. After 20 hours of operation, it was only 16 percent. Visible oil formation set in after 10 minutes at 230°C.

When the same catalyst was pretreated with mixed gas at 300°C., it gave a contraction of 17 percent within 2-1/2 hours. Oil was formed even then. By lowering the reaction temperature to 230°C., the contraction decreased to 6 percent, and after 70 hours, did not surpass 18 percent.

From these experiments, it is indicated that pretreatment with mixed gas at high temperatures is without advantage. It appears that oil formation was accelerated to some extent; however, the increase of contraction was not. As a matter of fact, we could observe that a catalyst pretreated in such a fashion behaved more unfavorably than the normally pretreated catalysts. Especially is this true for pretreatment at higher temperatures. This effect is understandable if one takes into consideration that the iron catalyst is comparatively sensitive at temperatures of around 250°C.

Influence of H_2 Pretreatment

As already mentioned, in contrast to cobalt and nickel catalysts, the iron catalysts can be used for the synthesis without a previous H_2 treatment. The latter, however, require a comparatively long period of induction. At a reaction temperature of 235°C., varying with the conditions of the synthesis, this time of induction lies between 20 and 30 hours. It takes approximately this length of time to produce the maximum contraction. It was desired to investigate whether this time of induction of the catalyst could be shortened by an H_2 treatment performed either at the reaction temperature or at some other higher temperature.

Hydrogen Treatment at Reaction Temperature, 235°-300°C. (Bahr)

All of the experiments carried out with this object in mind indicate that an H_2 treatment at the reaction temperature does not shorten the time of induction of the carrier-free catalyst. When a catalyst was treated for 1/2 hour or longer (up to 10 hours) with H_2, such a catalyst behaved just like a catalyst which was taken into operation immediately. No difference existed between the copper-containing and the copper-free catalysts. If the course of the H_2 pretreatment is followed closely, as the temperature increases slowly up to 200°C., the appearance of reaction water is noticed at around 100°C. This seems to indicate that the copper is being reduced. Water formation set in again at around 150°C. Obviously, at this temperature the reduction of the iron oxide and higher manganese oxides occurs. The reduction of these metals, however, does not proceed to the metallic state, but only to a lower oxide. In the case of manganese, MnO is produced.

H_2 Reduction at High Temperatures (Meyer)

A preliminary reduction of the Fe catalyst with H_2 at high temperatures caused a considerable decrease of the activity. A 5Fe-1Cu catalyst containing 1/4 percent K_2CO_3 which was taken into operation with mixed gas immediately, furnished 58 grams of liquid products. After 16 hours of reduction with H_2 at 450°C., followed by passage of mixed gas, a contraction of 14 percent was obtained after 1 hour. After 24 hours of further operation, the contraction decreased to 6.5 percent, and yellow products were formed. Since this catalyst was reduced by the H_2 treatment at 450°C. the deterioration of activity might have been caused by various reasons. First, the iron which was formed by the reduction at 450°C. might have sintered. Secondly, the high reduction temperature might have caused the iron and copper to form an alloy.

However, there is an indication that, in some cases, a reduction of the catalyst at high temperatures may be advantageous, as the following observation shows: A simultaneously precipitated Fe-Al catalyst (15 percent Al_2O_3 referred to iron), proved to be active when taken into operation with mixed gas immediately. After reduction with H_2 at 450°C., this catalyst yielded 27 percent contraction after 8 hours; however, it dropped to 9 percent after 6 days of operation. This finding is not in contrast to the statement just made, since, in the presence of Al_2O_3, the iron oxide is only reduced to a small degree to iron metal. This has been found to be true by experimental evidence not yet published. Furthermore, Al_2O_3 is capable of preventing sintering.

Since the catalyst did not contain any copper, a damaging effect due to alloy formation was not possible.

INFLUENCE OF ADDITION OF CARRIERS AND OF MODE OF ADDITION (Meyer)

The addition of carriers to cobalt and nickel catalysts is very important. It exerts a marked influence upon the activity and life of these catalysts. With iron catalysts, however, we found that the addition of carriers generally produces unfavorable results, except in those cases where the catalyst was mixed with alkali carriers, such as for instance, Stuttgart Mass. In these instances, activation is actually caused by the addition of the carriers. This increase in activation, however, should not be attributed to the presence of a carrier as such but to the fact that the carrier is alkaline. Such an increase in activity also could be accomplished by adding small quantities of K_2CO_3 to the catalyst free of carrier.

However, we have again investigated the question of the carrier, since in some cases the reaction differs when a carrier is added. Just as it is possible to direct the reaction of water formation, the possibility should exist of increasing the yields obtained from mixed gas and iron catalyst. In the next chapter, we shall report on these experiments.

Fe-Cu Carrier Catalysts from Ferrous Salts

The basic material chosen for a number of carrier catalysts had the composition 5Fe+1Cu. The preparation was accomplished as already described previously by precipitating the chlorides with Na_2CO_3. If alkalized with 1/4 or 1/8 percent K_2CO_3, this catalyst yielded 60 grams per cubic meter of mixed gas. Table 63 summarizes the results of experiments with iron catalysts containing carriers. It should be mentioned in advance that in no instance did the activity of a catalyst containing a carrier surpass the activity of a carrier-free catalyst. Generally, the carrier had an unfavorable influence on the performance of the catalyst. It was also observed that the mode of mixing the carrier and the catalyst was important. For experiment 2, the catalyst used in experiment 1, which had given 58 grams of liquid products, was mixed with kieselguhr. Thus, 4 grams of kieselguhr were added to every 10 grams of iron and mixed in a dry state. The catalyst required a time of induction of 4 days. This is understandable if one considers the larger volume of the catalyst and the better distribution and dissipation of the heat of reaction. Besides, the activity decreased faster than in the case of a kieselguhr-free catalyst. If the kieselguhr is added to the catalyst prior to precipitation, a more intimate mixture is obtained. This catalyst only furnishes a maximum contraction of 16 percent (experiment 3), which decreased to 13 percent after 4 days of operation. A preceding reduction by H_2 at 350°C. did not change the situation (experiment 4). The same catalyst, however, without K_2CO_3 addition (experiment 5) only yielded a contraction of 16 percent when taken into operation with mixed gas immediately. One can conclude from this that alkali in the presence of kieselguhr loses its activating properties. The two following experiments (6 and 7) show that diatomaceous earth reduces the activity of the iron-copper catalysts also. In experiments 8 to 10, sodium glass powder was added in various ways to a nonalkalized 5Fe-1Cu catalyst. In experiment 8, the sodium glass powder was mixed with a catalyst in a dry state, and in the course of 5 days' operation, 29-percent contraction was observed. The maximum yield amounted to 49 grams per cubic meter of mixed gas. From this, it appears that the activation caused by sodium glass powder is not as pronounced as the activation increase due to addition of K_2CO_3. If the addition of the glass powder is made before or after the precipitation (experiments 9 and 10), a maximum contraction of 26 percent is obtained in both cases after a long time of induction, and a yield of 40 grams is obtained. This increase in activity was less pronounced than when the glass powder was mixed in a dry state with the catalyst. For the sake of comparison, the catalyst was tested without glass powder addition under the same conditions (experiment 11). The maximum yield obtained was 28 grams.

Table 63.—Influence of addition of carrier and mode of addition (Precipitation of chloride with Na_2CO_3; 5Fe + 1Cu catalyst)

Experiment No.	K_2CO_3 content, percent	Carrier, 4 grams per 10 grams of Fe	Mode of addition	Reduction conditions	Maximum contraction, percent	Behavior of catalyst
1	1/4	Without	-	Immediately, mixed gas	33 230°	58 grams of liquid products.
2	1/4	Kieselguhr	Mixed dry afterward	Immediately, mixed gas	32 232°	51 grams of liquid products, induction time 4 days, faster decrease of activity than in the case without carrier.
3	1/4	Kieselguhr	Added before precipitation	Immediately, mixed gas	16 240°	Rapid decrease of activity, slight water formation.
4	1/4	Kieselguhr	Added before precipitation	H_2 350°	17 240°	Initially small water formation, only 10 percent contraction after 10 days.
5	Without	Kieselguhr	Added before precipitation	Immediately, mixed gas	16 240°	Initially small water formation, rapid decrease of activity.
6	Without	Diatomaceous earth powder	Added after precipitation	Immediately, mixed gas	16 236°	No water formation.
7	1/4	Diatomaceous earth powder	Added after precipitation	Immediately, mixed gas	22 236°	No water formation.

Table 63 (continued)

8	Without	sodium glass powder	Added afterward in dry state	Immediately, mixed gas	29 237°	49 grams of liquid products. Na-glass powder does not activate as well as K_2CO_3. Long time of induction.
9	Without	sodium glass powder	Added after precipitation	Immediately, mixed gas	26 237°	40 grams of liquid products. Very slow increase of activity. Mode of addition more unfavorable than dry state.
10	Without	sodium glass powder	Added before precipitation	Immediately, mixed gas	26 237°	40 grams of liquid products. Very slow increase of activity. Mode of addition more unfavorable than dry state.
11	Without	Without	-	Immediately, mixed gas	22 237°	28 grams of liquid products.
12	Without	Powdered silica gel	Added after precipitation	Immediately, mixed gas	15 240°	Slight activity.
13	1/4	Powdered silica gel	Added after precipitation	Immediately, mixed gas	13 240°	Slight water formation. No improvement when reduced with H_2 at 450° C.

Table 63 (Concluded)

14	1/4	Silica gel powder	Added dry afterward	Immediately, mixed gas		30 230°	56 grams of liquid products. When silica gel is afterward mixed in dry state, the latter remains indifferent.
15	Without	Asbestos meal 10 grams per 10 grams of iron	After precipitation	Mixed gas immediately. H_2 450°	10 21	250° 238°	Deterioration due to asbestos powder. Rapid decrease of activity.
16	1/4	Asbestos meal 10 grams per 10 grams of iron	After precipitation	Mixed gas immediately. H_2 450°	14 25	250° 238°	Deterioration due to asbestos powder. Rapid decrease of activity.

The addition of powdered silica gel caused an effect similar to that of kieselguhr (experiments 12 and 13). The alkalized, as well as the nonalkalized catalyst, showed the same behavior after addition of silica gel had taken place in a moist condition. The maximum contraction of 15 and 13 percent, respectively, could not be improved even after reduction with H_2 had been carried out at 450°C. When the silica gel was added dry to the alkalized catalyst, no effect was observed (experiment 14). By treating with H_2 at 450°C., only a short-lived increase in contraction, up to 21 and 25 percent, respectively, was observed.

Table 64 contains a few more experiments in which metal oxides were used as carriers. Although these metal oxides could not be considered as carriers, their effect is to be discussed here nevertheless, since these oxides were not mixed with the iron and copper by simultaneous precipitation but were added to the iron and copper separately after precipitation had been completed. Manganese oxide and zinc oxide decreased the activity of the alkalized as well as the nonalkalized iron-copper catalysts to the same degree (experiments 1-4). It should be mentioned that the alkalized catalysts possess a somewhat higher activity. The addition of Al_2O_3 lowered the activity of the iron-copper catalyst (experiments 5 and 6); no difference seemed to exist in the activity of the alkalized and nonalkalized catalyst. Finally, we investigated the influense of chromium oxide. Cr_2O_3 behaves indifferently irrespective of whether it was mixed with a catalyst in moist or in dry form. The yields with the alkalized and nonalkalized catalysts were of the same order of magnitude as without Cr_2O_3.

Summarizing the results, the following may be said about carriers: We have not succeeded in improving the yields by adding carriers to the iron-copper catalysts investigated in this work.

Fe-Cu-MnO Carrier Catalysts from Ferric Salts (Bahr)

We also investigated the effect which a carrier has upon Fe-Cu-MnO catalysts/that were precipitated from ferric salts. With these catalysts, we always used a larger quantity of carrier than we did with the Fe-Cu catalyst. The ratio of catalyst to carrier was 1:1. The quantity of carrier added was not without significance upon the activity of the catalyst. This was shown in the experiments on precipitated carrier catalysts.

Carrier Plus Decomposed Nitrates Catalysts

In early experiments we mixed the carrier material directly with the oxide powder obtained by decomposition of the nitrates. We added about 0.5 percent K_2CO_3, and the ratio of oxide powder and carrier was 1:1. As carriers, we used silica gel, kieselguhr, and ground Stuttgart mass. With this mode of addition, no difference in activity was noticed for the various carriers.

Later, we carried on investigations during which the carrier material was mixed with the nitrates before the decomposition. The resulting mass contained Fe-Cu-MnO catalysts and carrier in the ratio of 1:1. The necessary alkali (0.5 percent K_2CO_3 referred to the metal quantity) was added to the nitrates before the decomposition. The chief carriers used were Stuttgart mass (granulated and ground), silica gel, and kieselguhr. With this method of addition, no improvement over the carrier-free catalyst could be observed in any instance. The catalyst which contains Stuttgart mass or silica gel was approximately as active as the catalyst without carrier. It is interesting to note that the addition of kieselguhr caused deterioration of the catalyst, and rendered it almost inactive.

Table 64.—Influence of addition of carrier and mode of addition (Precipitation of the chloride with Na_2CO; 5Fe + 1Cu catalyst)

Experiment No.	K_2CO_3 content, percent	Carrier, 4 g. per 10 grams of Fe	Method of addition	Reduction condition	Max. contraction, percent	Behavior of catalysts
1	Without	MgO	Added after precipitation	Immediately mixed gas	12 235°	No water; slow increase of activity; MgO acts damaging.
2	1/4	do.	do.	do.	20 235°	do.
3	Without	ZnO	do.	do.	14 235°	No water formation; ZnO acts damaging.
4	1/4	do.	do.	do.	22 235°	do.
5	Without	Commercial Al_2O_3	do.	do.	13 235°	Deterioration by Al_2O_3; no water formation.
6	1/4	do.	do.	do.	13 235°	do.
7	Without	Commercial Cr_2O_3	do.	do.	22 230°	28 grams of liquid products.
8	1/4	do.	do.	do.	29 230°	51 grams of liquid products.[a]
9	Without	do.	Added dry	do.	15 230°	27 grams of liquid products.[a]
10	1/4	do.	do.	do.	30 230°	54 grams of liquid products.[a]

[a] Cr_2O_3 without effect.

The decomposition catalysts prepared in these two ways could be regenerated by oxidation with air at 250°C. with or without previous extraction of the paraffins.

Carrier Plus Precipitated Catalysts

By mixing a dry alkali-precipitated catalyst with a carrier such as silica gel or kieselguhr, catalysts were obtained which gave approximately the same percentage contraction as the carrier-free precipitated catalysts. (We found this information from earlier experiments.) The advantage derived from these precipitated catalysts was chiefly that the larger volume of catalyst contained a smaller quantity of metal. It should be mentioned, however, that the life of the catalyst was shorter in proportion to the smaller quantity of metal contents.

An essentially different picture resulted when the catalyst was precipitated on the carrier. When sodium hydroxide was the precipitant, we were not successful in obtaining active catalysts. For instance, a catalyst precipitated on kieselguhr by using NaOH proved to be practically inactive, even at 250°C. Also with Na_2CO_3- and K_2CO_3-precipitated kieselguhr, at first, very poorly active catalysts were obtained. Better results were found with asbestos, calcium carbonate, aluminum silicate, and powdered silica gel as carriers. The ratio of carrier material to metal quantity of the catalyst was 1:1, and these catalysts gave a contraction of 20 to 28 percent at 240°C. with 4 liters of mixed gas per hour.

The use of kieselguhr appeared undesirable in connection with precipitated iron catalysts. This is contrary to our experience with cobalt and nickel. Later we succeeded in essentially improving the kieselguhr precipitated iron catalysts without recognizing the reasons for the initial failure of this combination.

As mentioned in the section on "Experiments on Water Formation", we succeeded in conducting the synthesis over the course of partial water formation when using kieselguhr catalysts. This fact is of great significance with respect to the eventual possible increase in yield with the iron catalysts. For this reason, the Fe-Cu-MnO-kieselguhr catalysts with varying kieselguhr content have been subject to a thorough investigation (not yet concluded).

Preparation of Some Fe-Cu-MnO-Kieselguhr Catalysts

Ferric nitrate, copper nitrate, and manganous nitrate were dissolved in water. The quantity of water used was 60 times by weight that of the iron metal employed. The solution was heated to the boiling point, and then the required quantity of kieselguhr added. A hot solution of Na_2CO_3 was added to the hot nitrate-kieselguhr slurry under constant stirring. (The Na_2CO_3 solution contained the theoretical quantity of Na_2CO_3 + 5 percent excess in a tenfold weight of water.) The Na_2CO_3 solution was added to the nitrate-kieselguhr slurry in portions. After the precipitation was completed, the precipitate was filtered and washed six times with hot water. Each washing was equal to the volume of the original slurry. After the washing operation, the filtrate reacted only faintly alkaline. No alkalization of the catalyst was carried out. The catalyst was dried on the water bath and then further dried in the oven at 105°C. We have found it expedient not to take the catalyst into operation with mixed gas at once, but rather to heat it to reaction temperature with a stream of air just as in the case of the cobalt catalysts. Mixed gas was admitted after the water had been removed from the catalyst.

1(4Fe-1Cu-1MnO):1 Kieselguhr Catalyst

On account of the larger volume of the kieselguhr catalysts, we could not use 10 grams of iron as we did in the case of the carrier-free catalyst in earlier experiments. We used only 4 grams of iron. Visible oil formation began with a 1(4Fe-1Cu-1MnO):1 kieselguhr catalyst at a temperature of 235°C. The contraction after 5-1/2 hours was 16 percent, and after 22 hours it was 30 percent (maximum contraction). The catalyst yielded water from the very beginning. The section on "Experiments on Water Formation" describes the difference between the kieselguhr catalyst and the carrier-free catalyst for the same contraction. The kieselguhr catalyst converts only 66 percent of the CO at a contraction of 30 percent, whereas, metallic catalysts at a contraction of 30 to 32 percent convert up to 88 percent of the CO. The difference may be explained through the water formation of the kieselguhr catalysts.

A yield determination was not carried out for the 1:1 kieselguhr catalyst, since we found that the life of this catalyst was very short. After only 46 hours, a decrease of contraction set in. After 70 hours, the contraction had decreased to 20 percent.

Further experiments have indicated that a 1:1 kieselguhr catalyst is not readily reproduced. Some catalysts (of the same composition, apparently) only yielded a contraction of 15 to 20 percent at 235°C. The causes for this erratic behavior have not been discovered. We suspect that the alkali content of the catalysts has an effect. As already mentioned, no additional alkalization of the kieselguhr catalyst was carried out. The residual alkali apparently has an activating influence on the catalyst. Even after considerable washing, some residual alkali remains in the kieselguhr catalyst. It appears that this residual alkali in the 1:1 catalyst is variable.

We have endeavored to activate such an inactive 1:1 catalyst, for example, by boiling it with water to remove the possible unfavorable excess of alkali. No improvement of the catalyst resulted from this procedure. It should be mentioned here, however, that we did not succeed in removing any residual precipitating salts from a kieselguhr catalyst which was dried at 105°C. This may be seen from the following experiment.

A 1:1 kieselguhr catalyst precipitated with Na_2CO_3 was dried in the filter funnel and then subjected to drying in an oven at 105°C. The moist precipitate still reacted alkaline when tested with litmus. After drying, the catalyst was boiled for some time with water to remove residual alkali. Neither the aqueous filtrate nor the catalyst gave an alkaline reaction when tested with litmus after boiling. This indicates that the residual alkali was held firmly by the catalyst (the kieselguhr) after drying.

Assuming that an ineffective 1:1 kieselguhr catalyst contains too little alkali, we added additional alkali to the dried catalysts. Thus, we added 0.1 percent K_2CO_3 referred to the total weight of the catalyst. When the dried catalyst was treated with alkali, we found that the alkalization had no effect on the activity; neither was the activity affected when 0.1 percent K_2CO_3 was added to the still moist precipitate.

A decrease of the kieselguhr quantities did not improve the iron-kieselguhr catalyst any further.

$1(4Fe-1Cu-1MnO):0.5$ Kieselguhr Catalyst

A $1(4Fe-1Cu-1MnO):0.5$ kieselguhr catalyst was poorly active. It gave 11-percent contraction at 235°C. Strangely enough, no water formation was observed with this catalyst. This peculiarity of the carrier-catalyst was not pronounced with the small quantity of kieselguhr used.

$1(4Fe-1Cu-1MnO):2$ Kieselguhr Catalyst

Better yields were obtained with a $1(4Fe-1Cu-1MnO):2$ kieselguhr catalyst than with a 1:1 kieselguhr catalyst. With use of only 4 grams of iron in the catalyst charge and 4 liters per hour of gas at 235°C., the maximum contraction after 16 hours was 32 percent. At this point, the catalyst gave 47 grams of liquid products per cubic meter, in addition to 30 grams of water (including water vapor). Although this yield was smaller than that obtained with the carrier-free precipitated catalysts, it should be remembered that it was obtained with only 4/10 the customary charge of iron and also considerably smaller consumption of CO. In the present case, approximately 55 percent of the CO was used up. With complete CO conversion, a yield of 85 grams per cubic meter would result, as compared with a yield of 55 grams per cubic meter from a carrier-free catalyst. The total CO consumption was approximately 90 percent of the furnished CO. Here a yield of 61 grams would result for a complete conversion of the CO.

At 225°C. and with a 1:2 catalyst, a 20-percent contraction was still obtained for 4 liters per hour of gas and 26-percent contraction for 2 liters per hour. The corresponding yields were 27 and 36 grams, respectively, per cubic meter.

By using a larger quantity of catalyst, corresponding to 16 grams of iron, we succeeded with a 1:2 catalyst in increasing the yield further, and at the same time we were able to reduce the reaction temperature somewhat. The following results were obtained:

Temperature, °C.	Gas rate, liters per hour	Contraction, percent	Liquid products, grams per cubic meter
215	4.3	28	35
225	4.1	33	55

These results may be considered satisfactory from the point of view of CO usage, and the water formed during the reaction.

In most instances the 1:2 kieselguhr catalyst was reproducible. The life of the catalyst cannot be regarded as satisfactory. With a catalyst quantity corresponding to 4 grams of iron at an hourly gas rate of 4 liters after 120 hours at 235°C., a decreased contraction was observed. Apparently a reaction temperature of 235°C. is too high when working with kieselguhr catalysts. Better results were obtained at 225°C., although a smaller conversion was observed when the same quantity of iron (4 grams) was used.

No experiments have been conducted on a regeneration of the 1:2 catalyst.

1(4Fe-1Cu-1MnO):3 Kieselguhr Catalyst

When we used this catalyst, we could only charge the reactor with a quantity corresponding to 3.3 grams of iron, extending over a length of 30 cm.; the hourly gas rate was correspondingly decreased to 3 liters. The 1.3 catalyst at 225°C. gave a contraction of 28 percent, and a yield of 45 grams of liquid products per m^3. Forty grams of water per cubic meter were also formed, so that water and oil were produced in the ratio of 1:1.1. We investigated this catalyst at 235°C. and obtained only 30 grams of liquid products per cubic meter. This was attributed to the shorter life of the catalyst. The contraction decreased from 30 to 26 percent within 70 hours of operation.

1(4Fe-1Cu-1MnO):4 Kieselguhr Catalyst

Further dilution of the catalyst to 1:4 gave poor results. The time of induction of the catalyst was prolonged considerably. For example, with a quantity equivalent to 2 grams of iron, and 4 liters per hour of gas, at 235°C., 3-percent contraction after 46 hours, 9-percent after 118 hours, and only 12-percent after 142 hours resulted. At 245°C. this catalyst gave 20-percent maximum contraction. We did not make any yield determination for the experiments with the 1:4 catalysts on account of the low degree of conversion. Superficially judged, the catalyst behaved similarly to the catalysts previously described; that is, it had the ability to form water during the reaction from the very beginning.

With kieselguhr catalysts of composition 1:5 and 1:8, using the same normal catalyst layer length, only 1 and 0.5 grams of iron, respectively, could be used. With an hourly gas rate of 2 liters, these catalysts were tested at 250°C. and did not give a contraction surpassing 6 percent. Nevertheless, even these catalysts formed oil and water.

General Considerations on Kieselguhr-Precipitated Catalysts

As has been mentioned in previous paragraphs, the kieselguhr catalysts offer the possibility (even if only theoretical) of increasing the yields of liquid products, because they convert less CO to CO_2 than do the carrier-free catalysts. In order to apply the experience obtained with the kieselguhr catalysts on a technical scale, two disadvantageous properties of the catalysts must be overcome; namely, the unsatisfactory activity and the comparatively short life.

We have tried several means of increasing the activity of the kieselguhr catalysts. First of all, we studied the influence of subsequent alkalization. The catalysts, as previously mentioned, gave contractions up to 30 percent even without alkalization; in other words, contractions of the same order of magnitude as corresponded to the carrier-free catalysts. The CO conversion was, however, much lower on account of the prevalent formation of water. A series of experiments showed that the activity of such a carrier catalyst could not be improved by subsequent addition of alkali. It gave a maximum contraction of 30 percent. When alkali (K_2CO_3) was added in larger quantities (1 percent) to the already dried catalyst (at 105°C.) in some cases, we observed a damaging effect. Smaller additions were without influence. If the alkali was added to the still moist catalyst immediately after precipitation, additions of 0.1 to 0.2 percent did not cause any noticeable effect. With additions amounting to 0.5 to 1 percent, we observed CO_2 formation again.

These observations were especially apparent with catalysts precipitated with ammonia. The simultaneously or separately precipitated ammonium carbonate-kieselguhr catalysts of composition 1:1 to 1:2 were only mildly active in the absence of alkali. At 235°C. and 4 liters of gas per hour, they gave a contraction of 15 to 20 percent. When alkali was added, we observed that the formation of water decreased with increasing alkali content. With approximately 0.5 to 1 percent K_2CO_3, the visible water formation stopped.

We have, furthermore, tried to utilize the mixed gas to a greater extent with iron-kieselguhr catalyst (in one stage), by using correspondingly wider and longer catalyst tubes and larger quantities of catalyst. On the other hand, we tried to increase the conversion by reducing the gas rates and keeping the catalyst layer length at its normal value. A noticeable increase in contraction was observed in any case. The maximum contraction with kieselguhr catalysts reached in this manner was 37 percent. A more thorough investigation showed why a further increase in contraction is not possible. The CO under the given conditions was converted to a large degree, however, not to water, but to CO_2. It was therefore apparent that the carrier catalyst approached the behavior of the carrier-free metal catalyst when the conversion of the CO increased. In the section on "Experiments on Water Formation" the conversion conditions for a kieselguhr catalyst were described when the catalyst layer length varied. The experiment discussed there indicated that the water formed in the first section of the catalyst is decomposed again in the following sections and enters into a reaction with the CO according to the water-gas reaction.

In spite of the difficulties mentioned, we believe that by continuing the experiments with the iron catalysts containing kieselguhr we may eventually obtain yields that are higher than 55 grams of liquid products per cubic meter.

COURSE OF REACTION WITH IRON CATALYST (Bahr)

Between the carrier-free iron catalysts and the cobalt catalysts used for the gasoline synthesis, a remarkable difference exists; namely, the oxygen contained in the CO is chiefly converted into CO_2 when iron catalysts are used, whereas with cobalt catalysts (as well as nickel catalysts) water alone is formed. The course of the reaction with cobalt catalysts follows the following equation:

$$CO + 2H_2 = (CH_2) + H_2O,$$

whereas, for iron, the reaction chiefly proceeds according to:

$$2CO + H_2 = (CH_2) + CO_2.$$

This equation states that, with iron catalysts, for every molecule of hydrocarbons 1 molecule of CO_2 is produced; that is, in presence of iron catalysts only one-half of the CO goes to synthetic products of some nature. As already pointed out, the reaction with iron catalysts does not proceed exclusively according to the equation given above; but with varying experimental conditions, water may be formed. In general, it can be said that an iron catalyst converts larger quantities of the CO-oxygen to water when:

1. The reaction temperature is high.
2. The exit gas is rich in hydrogen.
3. The catalyst layer length is longer for a certain flow velocity, in other words, the smaller the gas rate for a given catalyst-layer length.

To show the differences between iron and cobalt catalysts more clearly, table 65 shows experiments with an Fe-Cu-MnO catalyst and a cobalt-manganese and a cobalt-thorium catalyst. The conversion of the various gas constituents was calculated in the following manner: The corresponding CO conversion into CO_2 is found from analysis of the reaction gases under consideration of the contraction. In this way, the percentage of the converted CO is also found. The difference of both quantities referred to 100 parts gives the percentage of CO used up. This comprises the total synthetic products, including the paraffin which remains in the catalyst. It also takes into consideration the carbon deposited on the catalyst as elementary carbidic carbon, originating from the CO. To ascertain how much oxygen (from the CO) went to water, we calculated at first how much CO-oxygen went into CO_2. The difference between this value as compared to 100 parts gives the percentage of oxygen converted into water, (including, perhaps, the oxygen-containing synthetic products). Although the calculations outlined here incorporate some inherent errors (for instance, the measurement of contraction in gas analysis), we have found it sufficient to obtain a general picture on the course of the conversion.

Table 65.—Comparison of gas conversion (mixed gas) with an Fe-Cu-MnO- and cobalt-manganese (15 percent) and cobalt-thorium (18 percent) catalyst[a]

	Fe-Cu-MnO + 1% K_2CO_3	Fe-Cu-MnO + 1% K_2CO_3	Cobalt-manganese	Cobalt-thorium
Temperature, °C.	220	220	195	190
Space velocity, liters per hour	4.4	2.2	4	4
Contraction, percent	30	36	70	70
CO conversion, percent to CO_2	43.4	40.5	1.1	1.6
Unchanged CO	7.2	6.5	15.6	12.3
Synthesis (difference)	49.4	53.0	84.4	87.7
O_2 conversion, percent to H_2O	6.0	12.5	83.3	86.1
Liquid products, grams per cubic meter	50.0	49.0	98.7	94.5
Reaction water, cc. per cubic meter[b]	16	28	—	—

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a/ Fe-Cu-MnO (4:1:1) + 1 percent K_2CO_3 was precipitated with NaOH from the nitrates. The cobalt catalysts were precipitated with soda from the nitrates, and the details are described in the experimental description of Dr. Koch (1932).

b/ Including the water content of the undried starting gas, amounting to 8 to 12 cubic centimeters per cubic meter.

The comparison of both catalyst species in table 65 shows that the cobalt catalysts form practically no CO_2. Hence, they convert almost all the CO-oxygen into water. In contrast, the iron catalysts form considerable CO_2, only half of the CO being used for the synthesis. Approximately 16 to 12 percent of the CO-oxygen is converted into water when iron catalysts are used. By comparing column 1 with column 2, it may be observed that by halving the gas rate, the water formation increased from 16 to 28 cc. of water per cubic meter of gas. On account of the large production of CO_2, the yields with iron catalysts are only approximately half those of the cobalt catalysts. This different reaction mechanism, which forms CO_2 rather than H_2O, is the chief reason why iron catalysts give lower yields than cobalt catalysts. The following example is explanatory: Referring to table 65, the cobalt-manganese catalyst acted on a mixed gas and gave 70-percent contraction. The reaction gas had the composition: CO_2 10.8 percent, olefins 3.2 percent, O_2 0.0, CO 13.6, H_2 32.8, hydrocarbons 16.2, carbon number 1.56, N_2 23.4.

It is evident that the catalyst uses CO and H_2 approximately in the ratio of 1:2, which is very close to the ratio of the two gases in the original mixed gas. The CO:H_2 ratio in the reaction gas is still 1:2.4. Theoretically, it is possible to remove the hydrocarbons from the reaction gas and obtain more complete conversion by recycling the unreacted components once more. An essentially different picture is obtained from the reaction-gas analyses of the iron catalysts. The catalyst mentioned in table 65 gave 30-percent contraction at 220°C. and a product gas of the following composition: CO_2 21.8 percent, olefins 0.7 percent, O_2 0.3, CO 3.2, H_2 58.8, hydrocarbons 5.4, carbon number 1.72, N_2 9.8.

Here, 93 percent of the CO was converted (3.2 percent CO in the end gas). The CO:H_2 ratio used up was, however, not in the ratio of 1:2. On account of the greater CO_2 quantity formed, more CO was consumed with respect to hydrogen than would correspond to 1CO:2H_2. Consequently, the final gas has a CO:H_2 ratio of 1:18.

Another experiment is discussed in which (on account of the low reaction temperature of 210°C.) a somewhat larger part of the CO was not converted. For this experiment (table 66, No. 2), the following end-gas analysis was obtained with 26-percent contraction: CO_2 18.2, olefins 0.3, O_2 0.2, CO 9.0, H_2 59.8, hydrocarbons 2.5, carbon number 2.75, N_2 10.0.

The analysis shows that the shifting of the ratio of CO:H_2 in the end gas ~~is very~~ considerable for this catalyst (approximately 78 percent of the CO was converted). The ratio is only still 1:6.6 in the final gas.

The following experiment shows finally that shifting the ratio of CO:H_2 was noticeable in the first stages of the reaction. An Fe-Cu-MnO catalyst was tested at 220°C., and it gave 10-percent contraction at a certain gas rate. The reaction gas had the following composition: CO_2 8.1 percent, olefins 0.0 percent, O_2 0.4, CO 21.4, H_2 60.1, hydrocarbons 2.8, carbon number 1.43, N_2 7.2.

Although only 26.5 percent of the CO was converted, the CO_2:H_2 ratio in the reaction gas shifted from 1:2 (mixed gas) to 1:2.8.

In contrast to the cobalt catalyst which uses CO and H_2 approximately in the ratio of 1:2, the gas composition changed very rapidly all along the course of the reaction tube when iron catalysts were used. This was true even for very small contractions and became more pronounced as the conversion increased. With an iron catalyst, therefore, only the first zones of the catalyst received a gas of the original composition. The succeeding zones received gases that were more and more enriched in H_2 and leaner in CO. To convert such a gas to liquid products different reaction conditions obviously are necessary than were required for the original gas.

Considering the comparatively high CO usage with iron catalysts, it is obvious that a gas richer in CO than ordinary mixed gas should be used. This is evident from the equation, $2CO + H_2 = CO_2 + CH_2$. We have, however, found that the activity of the iron catalyst decreases very rapidly when such a gas was used. The activity could not be maintained, even when the gas rate was reduced. Even when water gas was employed, this rapid decrease of activity was noticeable. The shifting of the $CO:H_2$ ratio in the gas was the reason for not resorting to recycling to obtain a higher yield of liquid products and more complete conversion.

In the following, the product gas analyses are summarized, as they were obtained with an iron-copper-manganese catalyst at a temperature of 190° to 230°C. To facilitate working at 190°C., a larger quantity of catalyst was used for this experiment. The catalyst used corresponded to 120 grams of Fe-Cu-MnO. The analyses show how, comparatively independently of the reaction temperatures, the final gases become richer in H_2 and leaner in CO.

Temperature, °C.	Gas rate, liters per hour	Contraction, percent	CO_2	Olefins	O_2	CO	H_2	Hydrocarbons	Carbon No.	N_2
190	1.5	20	14.8	0.5	0.2	12.8	61.5	1.5	2.33	8.8
200	2.7	24	19.8	.2	.2	6.8	61.1	2.5	2.20	9.4
220	3.9	32	22.4	.3	.1	1.7	60.0	6.6	2.55	8.9
230	4.6	33	21.6	.6	.2	1.9	55.4	10.5	1.46	9.8

EXPERIMENTS ON WATER FORMATION (Bahr)

As mentioned in the section on "Course of Reaction with the Iron Catalyst", the smaller yields obtained with iron catalysts as compared with cobalt catalysts were caused chiefly because the reaction yields considerable CO_2 rather than water. It has already been pointed out that, with iron catalysts under certain conditions, the formation of water may be observed. In the following series of experiments, we attempted to prevent the CO_2 formation on the catalyst in order to obtain a higher yield of liquid products. We investigated the following:

1. The influence of gas composition (of $CO:H_2$ ratio) upon the formation of CO_2 and water.
2. The influence of alkali content upon the CO_2 formation.
3. The CO_2 formation when using a CO_2-containing initial gas.
4. The CO_2-water formation on iron catalysts containing carriers.

Influence of Gas Composition ($CO:H_2$ Ratio) Upon CO_2 and H_2O Formation

During the following experiments, Fe-Cu-MnO (4:1:1 containing 1 percent K_2CO_3) catalysts were used. They were prepared by precipitation from the nitrates with sodium hydroxide. The comparatively high alkali content (1 percent) had an advantageous effect on NaOH-precipitated catalysts. Later, however, we used catalysts precipitated with soda, and found that these catalysts produced still better results. These catalysts should be only weakly alkalized, containing no more than 0.1 to 0.2 percent K_2CO_3.

Experiments with Mixed Gas

The mixed gas used had the following composition: CO_2 2.2 percent, Olefins 0.0 percent, O_2 0.0, CO 30.6, H_2 58.1, hydrocarbons 1.5, N_2 7.6 [illegible].

The ratio of CO:H_2 was 1:1.9. To start with, we investigated the influence of reaction temperature on the course of the CO conversion in the mixed gas. To extend the experiments and to be able to vary the temperature and gas velocity considerably, a comparatively large catalyst charge (120 grams to 80 grams of iron) was used. The results of the experiments are given in table 66. They are arranged in the order of increasing reaction temperatures. The table shows, first, that at low temperatures (200°-210°C.), a comparatively large quantity of the CO remains unconverted. This is caused mainly by the poor activity of iron catalysts in this temperature range. In addition, an iron catalyst at 200° or 210°C. requires a longer period of induction than 30 to 60 hours. The catalysts were first allowed to act at 220°-230°C. until they gave a contraction of 20 to 25 percent. Thereafter the temperature was lowered. The table then shows how, with increasing reaction temperature, the quantity of CO converted to CO_2 decreased, as compared to the CO required for the synthesis. At 200° to 210°C., approximately the same amount of CO was converted to CO_2 as was converted to hydrocarbons. At these temperatures, no water was formed, all of the oxygen converting to CO_2. At 220°C., 6 percent more of the CO was used for the synthesis proper; at 230°C., 10 percent; and at 240°C., 21 percent more CO was used for the synthesis than was used for CO_2 formation. At the same time, increasing quantities of water were formed with the oil. The horizontal row indicates what part of the CO-oxygen was converted into water at the various temperatures. Experiments 6 and 7 show the influence of the space velocity.

At a space velocity of 9.8 liters of gas per hour and 240°C., approximately 40 percent of the CO went to CO_2, whereas 54 percent was used for the synthesis. With 1.6 liters of gas per hour, approximately one-third of the CO went to CO_2, and 60 percent went into the synthesis. From the table it is not apparent that the yield of liquid products was increased, however. This is apparent by comparing experiments 3 and 5. For experiment 3, 49 percent and for experiment 5, 59 percent of the CO was used for the synthesis. However, the yield of liquid products for both experiments was 50 and 49.5 grams per cubic meter of gas, respectively.

If the "theoretical yield" of gaseous, liquid, and solid hydrocarbons is calculated for the synthesis on the basis of the CO contents (expressed in grams of hydrocarbons per cubic meter of gas), on comparing these calculated yields with the liquid products obtained, the difference between the total yield and the liquid-product yield should account for the gaseous hydrocarbons and other compounds formed. The table shows that, for reaction temperatures of 200° to 210°C., comparatively larger quantities of products other than liquid were formed. At 200°C. they were approximately 51 grams, and at 210°C. they amounted to 40 grams per cubic meter. Since the reaction gas from these experiments contained a comparatively small amount of methane hydrocarbons, one was justified in assuming that during the reaction larger quantities of paraffin remained in the catalyst when the operating temperature was lower. For the following experiments, which were conducted between 220° and 240°C., we observed increasing amounts of paraffin hydrocarbons in the reaction gas. The carbon number of the

Table 66.—Influence of temperature upon CO conversion (mixed gas) with Fe-Cu-MnO catalysts containing 1 percent K_2CO_3

	1	2	3	4	5	6	7
Temperature, °C.	200	210	220	230	240	240	240
Hours of operation	263	191	436	602	741	864	858
Space velocity, liters per hour	2.7	4.0	4.4	4.6	3.4	9.8	1.6
Contraction, percent	24	26	30	32	36	30	38
CO conversion, percent to CO_2	41.8	38.6	43.4	41.8	37.7	39.4	35.5
Unchanged CO	17.0	22.1	7.2	6.5	3.8	6.5	4.5
Synthesis (difference)	41.2	39.3	49.4	51.7	58.5	54.1	60.2
O_2 conversion, percent to H_2O	.6	.7	6.0	9.9	20.8	14.7	24.7
Reaction water, cc per cubic meter[a]	12.3	10.7	16.4	26.5	42.9	26.7	n.b.[b]
Liquid products, grams per cubic meter	22.7	29.6	50.0	49.7	49.5	n.b.	n.b.
Calculated theoretical yield, grams of hydrocarbons per cubic meter	73.5	69.4	87.5	92	99.8	92.2	102.7
Reaction gas:							
CH_4 content, percent	2.6	2.5	5.4	10.5	10.9	8.1	14.3
Carbon number	2.20	2.75	1.72	1.46	1.37	1.34	1.46

[a] Including water content of the undried starting gas.

[b] n.b. = not observed.

hydrocarbons decreased with increasing temperature. The difference between the calculated yield and the experimental yield of liquid product yield obviously was caused chiefly by the increased formation of gaseous hydrocarbons. The gaseous hydrocarbons may be gasol or methane. If experiments 3 and 5 are compared with each other, one observes that during experiment 3, 37 grams of products other than liquid were formed, and for experiment 5, 50 grams of synthesis products were formed which were not liquid. The analyses of the reaction gases show that during experiment 5 approximately twice as many paraffin hydrocarbons were formed as during experiment 3. By raising the temperature the conversion of the CO during the synthesis appears more complete. Obviously, however, this larger conversion did not cause an increase in yield of liquid products but only increased the portion of gaseous hydrocarbons formed.

In particular, we want to refer to experiments 6 and 7 which are listed in the table. From them, the influence of the space velocity upon the nature of the conversion at 240°C. may be observed. By reducing the hourly throughput from 9.8 to 1.6 liters, the contraction increased from 30 to 38 percent and 60 percent of the CO was consumed during the synthesis. From these data, a theoretical yield of 103 grams of hydrocarbons per cubic meter of gas can be calculated. No yield determination was made. However, it is apparent from the gas analysis that for this slow gas throughput, a large amount of gaseous hydrocarbons formed (14.3 percent paraffin hydrocarbons).

From a further series of experiments, one can observe that, for still lower reaction temperatures, the gasoline formation on the iron catalyst proceeds predominantly by way of CO_2 formation. The results of the experiments are tabulated in table 67. In order to lower the experiment temperature considerably, we used for this experiment an Fe-Cu-MnO catalyst which contained 5 percent K_2CO_3 (90 grams, 60 grams of iron). We initiated the catalyst at 220°C., and thereafter the temperature was lowered gradually—the lowest experiment temperature was 170°C. For this temperature and a gas rate of approximately 1 liter per hour, a contraction of 11 percent was still observed. On account of the low throughput, we decided not to make a yield determination, and we merely analyzed the end gas.

Table 67.—CO conversion (mixed gas) on Fe-Cu-MnO + 5 percent K_2CO_3 at low temperatures

	1	2	3	4
Temperature, °C.	220	200	190	170
Hours of operation	41	48	140	185
Space velocity, liters per hour	4.0	4.1	1.2	1.1
Contraction, percent	31	22.1	22.8	10.8
CO conversion, percent to CO_2	44.5	37.6	44.0	19.3
Unchanged CO	6.2	23.8	10.6	61.0
Synthesis (difference)	49.3	38.6	45.4	19.7
O_2 conversion, percent to H_2O	4.8	1.0	1.4	.4
O_2 conversion, percent to CO_2	89.0	75.2	88.0	38.6

Table 67 shows (as is already apparent from earlier experiments) that in the range of the low reaction temperatures, the reaction proceeds by way of CO_2 formation. For instance, at 170°C. the CO quantity converted to CO_2 was approximately the same as the CO_2 quantity converted to hydrocarbons. This condition does not change appreciably at 190° to 200°C.; but at 220°C., we could observe that the quantity of CO converted to hydrocarbons was larger than the quantity of CO converted to CO_2. At this temperature, too, we observed the formation of small quantities of water. Originally, we were inclined to believe that the differences in the reaction mechanism between iron and cobalt catalysts was mainly due to the higher reaction temperatures that the iron demands. The above experiments indicate, however, that the iron catalyst under investigation did not form increasing quantities of water when it was permitted to operate in the reaction temperature range of the cobalt catalysts. In fact, we observed the opposite tendency; namely, that in this temperature range CO_2 was formed exclusively. The lower the reaction temperature, the more CO_2 was formed.

Experiments with H_2-rich Gas

For the following experiments, instead of using mixed gas, a H_2-rich gas was employed to determine whether the CO_2 formation could be suppressed by using a large excess of H_2. The gas employed had a $CO:H_2$ ratio of 1:4.2. The theoretical yield of liquid products may be calculated to be 208 grams of hydrocarbons per cubic meter. The composition of the gas was as follows: CO_2 0.0, Olefins 0.0, O_2 0.0, CO 18.6, H_2 79.2, no paraffin hydrocarbons, N_2 2.2.

The quantity of catalyst used was 60 grams, which was equivalent to 40 grams of iron. The experimental results are arranged according to reaction temperatures in table 68.

Table 6e.—CO conversion when using H_2-rich gas ($CO:H_2$ = 1:4.2) on Fe-Cu-MnO catalysts containing 1 percent K_2CO_3

	1	2	3	4	5
Temperature, °C.	200	210	220	230	240
Hours of operation	593	473	353	113	287
Space velocity, liters per hour	4.0	4.1	3.9	3.7	7.9
Contraction, percent	19.7	20.6	23.1	25.0	22.7
CO conversion, percent to CO_2	32.8	45.1	41.4	42.5	41.4
Unchanged CO	28.0	3.8	6.5	7.5	7.0
Synthesis (difference)	39.2	51.1	52.1	50.0	51.6
O_2 conversion, percent to H_2O	6.4	6.0	10.7	7.5	10.2
Reaction water, cc per cubic meter[a/]	16.6	24.1	28.3	25.4	28.8
Liquid products, grams per cubic meter	16.2	35.1	35.9	29.9	29.3
Reported theoretical yield, grams CH_2 per cubic meter	42.6	55.5	56.5	54.0	56.0
Reaction gas:					
CH_4 content, percent	3.5	2.2	1.3	2.6	1.9
Carbon number	1.0	2.27	2.08	1.65	1.89

a/ Including water content of the undried starting gas.

In general, table 6e shows that an H_2-rich gas does not give better results as far as the suppression of CO_2 formation is concerned. By using an H_2-rich gas, the water formation seems to set in somewhat earlier. We already could observe water at 210° and 200°C. However, at higher temperatures, as for instance, 230° and 240°C., the reaction water formation predominates. Comparison with table 66 (mixed gas experiments) shows that an H_2-rich gas does not give any better results than a mixed gas as far as water formation is concerned at higher temperatures. Some additional interesting information may be obtained from table 68. It appears that an H_2-rich gas tends to produce comparatively large quantities of gaseous hydrocarbons in addition to the usual liquid products, as may be seen by comparing the calculated theoretical yields with the observed yields of liquid products. It is remarkable also that for low temperatures (200°C.) considerable difference exists between both values. In general, the experiments may be summarized as follows: When using an H_2-rich gas, the degree of conversion of CO to liquid products was not larger than with mixed gas. With a mixed gas containing 30 percent of CO (compare table 66), on the average, fifty grams of liquid products per cubic meter were obtained. On a CO_2-free basis, this figure corresponded to a degree of liquefaction of 57 percent. For the H_2-rich gas (18.6 percent CO), the yields amounted to 35 to 36 grams per cubic meter, which corresponds to a degree of liquefaction of 65 to 66 percent on a CO_2-free basis.

In general, we want to emphasize the percent contractions obtained by using the H_2-rich gas. On the average, we observed 20 to 23 percent, that is, numerically it was approximately 2 to 5 percent above the CO contents of the initial gas. The situation was similar for the mixed gas. With mixed gas, the average maximum contraction was 30 to 35 percent, with an initial CO content of 28 to 30 percent in the synthesis gas.

It should be mentioned here that the iron catalysts required a longer time of induction when used with H_2-rich gases compared to the time of induction for mixed gas.

The experiments with H_2-rich gas were repeated with another Fe-Cu-MnO catalyst containing 1 percent K_2CO_3 (8 grams of iron), to determine how the gas composition shifts at high temperatures (up to 260°C.). We obtained the following data (table 69). With increased temperature, the CO_2 content diminished, and for the maximum temperature (260°C.) it decreased to 35 percent of the CO originally employed. At this point, 57 percent of the CO was used for the synthesis. Similar results were observed earlier with mixed gas at 240°C., when larger quantities of catalyst were employed (compare table 66, experiment 5).

Table 69.--CO conversion with H_2-rich gases ($CO:H_2 = 1:4.2$) on Fe-Cu-MnO catalysts containing 1 percent K_2CO_3, for a temperature range of 230° to 260°C.

	1	2	3	4
Temperature, °C.	230	240	250	260
Space velocity, liters per hour	3.7	4.0	4.2	4.0
Contraction, percent	21.3	19.8	24.4	25.8
CO conversion, percent to CO_2	41.3	44.0	39.7	34.9
Unchanged CO	9.0	6.4	7.4	7.9
Synthesis (difference)	49.7	49.6	52.9	57.2
O_2 conversion, percent to H_2O	8.4	12.8	13.2	22.3

Experiments with CO-Deficient Gas

The conditions for conversion were investigated again with a starting gas containing CO and H_2 in the ratio of 1:8.5. The gas had the following composition: CO_2 0.0 percent, Olefins 0.0 percent, O_2 0.3, CO 10.4, H_2 88.3, no hydrocarbons, N_2 1.0.

The theoretically possible yield for this gas was 61 grams of hydrocarbons per cubic meter.

The experiments carried out in this connection immediately followed those described in table 68. The same catalyst was used without previous regeneration. The catalyst (60 grams = 40 grams of iron) at this time already had been in operation for 980 hours without decrease in activity. By using the CO-deficient gas, the experimental results of table 70 were obtained.

Table 70.--CO conversion for a CO-deficient gas ($CO:H_2 = 1:8.5$) on Fe-Cu-MnO catalysts containing 1 percent K_2CO_3

	1	2
Temperature, °C.	220	220
Space velocity, liters per hour	4.3	5.3
Contraction, percent	13.9	18.2
CO conversion, percent to CO_2	34.6	27.0
Unchanged CO	8.6	9.6
Synthesis (difference)	56.7	63.4
O_2 conversion, percent to H_2O	22.1	36.4
Liquid products, grams per cubic meter	n.b.[a]	19.7
Reaction water, cc per cubic meter	--	23.2

[a] n.b. = not determined.

Table 70 shows that it was possible to decrease the conversion of CO to CO_2 to a value of 27 percent when using a large excess of H_2. For the same experiments, 63 percent of the CO was converted to synthesis hydrocarbons. Roughly, 36 percent of the available oxygen in the CO was converted into water. A conversion of 63 percent of the CO to synthesis products would correspond to a yield of 39 grams of hydrocarbons per cubic meter. The determination showed, however, that only 20 grams of liquid products per cubic meter would form; hence, an approximately equal quantity of other synthesis products was produced. The reaction gas contained 2.3 volume-percent of paraffin hydrocarbons with a carbon number of 1.78. The yield of approximately 20 grams of liquid products would correspond to a degree of liquefaction of 65 percent, referred to half of the CO quantity in the original gas. As already pointed out, 65 to 60 percent of the liquefaction was reached with H_2-rich gas. One can see, therefore, that with a large excess of H_2, it was not possible to exceed this degree of liquefaction.

The result of the series of experiments showing the influence of gas composition ($CO:H_2$ ratio) upon the CO_2 formation may be summarized as follows: By using larger quantities of catalyst (or smaller gas throughputs) and working at higher reaction temperatures or using an H_2-rich original gas, one succeeds in directing the reduction of CO partly by way of water formation (for an Fe-Cu-MnO catalyst). In the most favorable case, 20 to 36 percent of the oxygen contained in the CO could be converted into water. The ratio of the CO converted into CO_2 and the CO converted into synthesis products was 1:2.3 for the most productive case (table 70, experiment 2). An essential increase in the yield of liquid products was, however, not obtained with the formation of water. The degree of liquefaction obtained was 57 percent when mixed gas was used, and for an H_2-rich gas (up to a $CO:H_2$ ratio of 1:8.5), 65 to 66 percent liquefaction was obtained, on a CO_2-free basis.

From the experiments reported here, it may be concluded that the formation of water obviously proceeds in a different manner than with cobalt catalysts. Water did not appear before a certain dilution of the CO in the reaction gas was reached. When H_2-rich gases were used, this condition was met at once, and the formation of reaction water (visible separation of water in the receiver) was generally observed when a contraction of 25 percent was reached. Obviously, the CO was converted in the first sections of the apparatus to such a degree that the succeeding sections of the unit were charged with an H_2-rich gas. Such a gas, however, furnished predominantly gaseous hydrocarbons at the temperatures in question. Therefore, the yield of liquid products did not increase essentially when water formed.

Influence of Alkali Content Upon CO_2 Formation, Using Iron Catalysts

To acquire full activity, the carrier-free Fe-Cu-MnO catalysts required activation with fixed alkali. This was contrary to observations with cobalt catalysts. It could be assumed that the different course of the reaction with the precipitated iron catalysts resulted from the alkali content of the catalyst. (By different course of the reaction, CO_2 formation is meant.) This may refer to the alkali (K_2CO_3) which was added after the catalyst was precipitated, or it may refer to the residual alkali content of the precipitated catalysts (such as Na_2CO_3). Even if the iron catalysts were washed thoroughly, considerable quantities of Na_2CO_3 remained.

To investigate this point, a number of Fe-Cu-MnO catalysts were prepared in which ammonium carbonate was used as precipitant. The method of preparation and the general behavior of these poorly-active catalysts were described in the section on "Iron-Copper Three-Component Catalysts Prepared from Ferric Compounds". In the following, we shall consider the effect of freedom from fixed alkali on the formation of water. In table 71 experiments with two Fe-Cu-MnO (4:1:1) ammonium carbonate precipitated catalysts are described.

Table 71.—CO conversion (mixed gas) with Fe-Cu-MnO catalysts precipitated with ammonium carbonate

	1 Fe:Cu:MnO 10:2.5:2.5	2 Fe:Cu:MnO 40:10:10
Temperature, °C.	235	235
Throughput, liters per hour	4.1	2.0
Contraction, percent	17.4	32
CO conversion, percent to CO_2	13.8	44.4
Unchanged CO	61.5	8.0
Synthesis (difference)	24.7	47.6
O_2 conversion, percent to CO_2	27.6	88.8
O_2 conversion, percent to H_2O (difference)	10.9	3.2
Reaction gas, volume percent:		
CO_2	6.2	20.3
CO	22.0	3.5
H_2	57.3	53.9
CH_4	4.5	10.2
Carbon number	1.51	2.34

The experiments listed in table 71 indicate that an immediate relationship between the alkali content of the catalyst and CO_2 formation during the synthesis did not exist, as those catalysts which were free from alkali produced predominantly CO_2. The catalyst mentioned in the first column was an exception. This catalyst produced water when the contraction was only 12 percent. Eleven percent of the CO converted went to water, whereas 28 percent went to CO_2. Next we tried to increase the conversion of the CO by using larger quantities of catalyst and by decreasing the gas throughputs (experiment 2). However, here, also CO_2 formed almost exclusively. For experiment 1, the $H_2O:H_2$ ratio was 1:2.5. For experiment 2, it had increased to 1:2.8. For experiment 1, the end gas showed a ratio of $CO:H_2$ of 1:2.6. For experiment 2, however, this same ratio was 1:15.4.

Experiments on CO_2 Formation on Iron Catalysts When Using a CO_2-Rich Starting Gas

In the following, we attempted to suppress the formation of CO_2 on iron catalysts by adding certain quantities of CO_2 to the starting gas. For these experiments, we employed Fe-Cu-MnO catalysts (10:2.5:2.5), which were precipitated with soda and contained 0.1 percent K_2CO_3. The original analysis is given in table 72; the $CO:H_2$ ratio was 1:1.8. This was somewhat low. Of several experiments, which on the whole gave good results, only two are discussed here.

Table 72.—Product gas analyses by using a CO_2-rich starting gas

Experiment No.	Temperature, °C.	Throughput, liters per hour	Contraction, percent	Composition of product gases, percent							
				CO_2	Olefins	O_2	CO	H_2	Methane	Carbon No.	N_2
1	235	4.1	26.4	28.9	1.5	0.1	7.8	56.4	1.6	1.63	3.7
2	240	4.0	32.8	28.7	1.2	.2	8.0	54.4	3.9	1.38	3.6
	Initial gas			10.3	.0	.0	30.8	55.1	-	—	3.8

By comparing the two product-gas analyses with the initial gas, it can be said qualitatively that the addition of CO_2 to the starting gas did not impede the CO_2 formation. In both cases, enrichment in H_2 occurred in the end gas. The ratio of the residual CO and H_2 shifted to 1:7.2 for experiment 1 and for experiment 2 to 1:6.8, showing that for experiment 1, at least, CO_2 formation was not influenced by the CO_2 addition to the starting gas. Neither was more CO-oxygen converted to water. No reduction of CO_2 formation from CO was observed. Experiment 2 shows somewhat better results. The ratio of H_2O to CO_2 was 1:2.4. No increase in the yield of liquid products was observed during this experiment. 44.5 Grams per cubic meter were obtained. This corresponds to a conversion of 55 percent, considering the low H_2 content of the starting gas. The degree of liquefaction just mentioned was referred to one-half of the usable CO in the starting gas. The course of CO conversion, using a CO_2-rich starting gas is shown in Table 73.

Table 73.—Course of CO conversion by using a starting gas containing CO_2

	Experiment 1 (235°C.)	Experiment 2 (240°C.)
CO conversion, percent to CO_2	35.7	29.2
Unchanged CO	18.5	17.5
Synthesis (difference)	45.8	53.3
O_2 conversion, percent to CO_2	71.4	58.4
O_2 conversion, percent to H_2O (diff.)	10.1	24.1
H_2O:CO_2	1:7.2	1:2.4

CO_2 and Water Formation on Iron-Carrier Catalysts

An essentially different result with respect to CO_2 and H_2O formation was observed when metal-carrier catalysts were used instead of the metal catalysts alone. We investigated carrier catalysts in which kieselguhr and the active constituents were coprecipitated with soda. We also investigated precipitated catalysts in which the carrier material (tonsil) was added after precipitation. (The term "tonsil" refers to a silica clay which is used as a catalyst carrier.)

Fe-Cu-MnO-Kieselguhr Catalysts

A description of the method of the preparation and the behavior of the kieselguhr precipitated catalysts has been presented in the section on "Influence of Addition of Carriers and of Mode of Addition". In general, we limited ourselves to investigating the influence of the kieselguhr addition upon the CO_2 and H_2O formation. When a precipitated catalyst (Fe-Cu-MnO, 4:1:1), precipitated with soda, and containing 6 grams of kieselguhr was taken into operation, water formation began simultaneously with oil formation from the beginning. The temperature was 235°C., and the gas throughput was 4 liters of mixed gas per hour. For the metal catalysts already described, the formation of water could be detected only after higher contractions were observed. The carrier-catalyst gave 30-percent contraction after 22 hours—in other words, just as much as the carrier-free catalysts gave in the same time. The product gas had the following composition:

	CO_2	Olefin	O_2	CO	H_2	Methane	Carbon No.	N_2
Kieselguhr catalyst, 30-percent contraction	11.5	1.1	0.2	13.9	59.4	2.7	3.37	11.2
Metal catalyst, 32-percent contraction	17.9	1.3	.1	5.0	59.5	4.8	1.32	11.4

The kieselguhr catalyst, upon comparison with a carrier-free precipitated metal catalyst (precipitated with soda), was shown to give smaller quantities of CO_2 at approximately the same contraction. Furthermore, a larger proportion of the CO remained unconverted. The final gas did not show such pronounced shifting of the ratio of CO to H_2. The ratio was 1:4.3 for the kieselguhr catalyst, as compared to 1:11.9 for the metal catalyst.

Better insight into the gas conversions may be obtained from table 74.

Table 74.—Gas conversion (mixed gas) with an Fe-Cu-MnO (4:1:1) catalyst precipitated with Na_2CO_3 and gas conversion for kieselguhr catalysts

	Metal catalyst	Kieselguhr catalyst
Temperature, °C.	235	235
Space velocity, liters per hour	4	4
Contraction, percent	32.4	30.0
CO conversion, percent to CO_2	38.2	26.1
Unchanged CO	11.7	33.8
Synthesis (difference)	50.1	40.1
O_2 conversion, percent to CO_2	76.4	52.2
O_2 conversion, percent to H_2O (difference)	11.9	14.0
$H_2O:CO_2$	1:6.4	1:3.7

A comparison between the two series of experiments shows that the experiment with the kieselguhr catalyst produced more water. For 66-percent conversion of the CO, the ratio of $H_2O:CO_2$ formed was 1:3.7, whereas, with the unsupported metal catalyst, at 88-percent conversion of the CO, the ratio was 1:6.4. Approximately six times as much oxygen went to CO_2 as to H_2O in the latter case.

We did not make a yield determination of liquid products for the experiments described above. From calculations we observed that despite increased water formation on the kieselguhr catalysts (on account of the lower gas conversion), an increase in yield did not occur.

Further experiments confirmed the observation of increased water formation on the kieselguhr catalysts. These experiments to some extent also gave better results on the conversion relationships of CO.

Table 75 shows the results of two further experiments. One of the tests was conducted with a catalyst somewhat leaner in copper.

Table 75.—Gas conversion (mixed gas) on kieselguhr-precipitated catalysts

	1 Fe-Cu-MnO 4:1:1 a/ kieselguhr	2 Fe-Cu-MnO 4:0.2:1a/ kieselguhr
Temperature, °C.	235	235
Space velocity, liters per hour	4	4
Contraction, percent	32.4	29.2
Reaction gas, volume percent:		
CO_2	14.4	7.6
Olefins	.8	.0
O_2	.2	.0
CO	11.2	18.5
H_2	54.2	57.1
Hydrocarbons	5.9	2.8
Carbon number	1.73	2.25
N_2	13.3	14.0
CO conversion, percent to CO_2	28.1	15.5
Unchanged CO	24.5	44.3
Synthesis (difference)	47.4	40.2
O_2 conversion, percent to CO_2	56.2	31.0
O_2 conversion, percent to H_2O (difference)	24.5	24.7
$H_2O:CO_2$	1:2.3	1:1.3

a/ The ratio of Fe-Cu-MnO:kieselguhr is 1:1.

With catalyst 1, a conversion of 76 percent of the CO was obtained, and only 2.3 times more CO_2 was formed than water. With catalyst 2, only 1.3 times more CO_2 was formed than water at a total CO conversion of 56 percent, however.

At any rate, for these experiments the larger part of the CO-oxygen still went to CO_2. Therefore, we tried to suppress CO_2 formation by using catalysts of still higher kieselguhr content and by lowering the reaction temperature.

Maximum conversion possible for these experiments has not been estimated, because the kieselguhr-rich catalysts occupied a large volume in the reaction tube and thus permitted the presence of small quantities of Fe-Cu-MnO. In table 76, two catalysts rich in kieselguhr and precipitated with Na_2CO_3 were mentioned. The first catalyst contained 2 parts of kieselguhr per part of Fe-Cu-MnO, whereas the second contained 3 parts of kieselguhr per part of active constituents.

From table 76 it is apparent that the 1:2 kieselguhr catalyst did not produce more water than the 1:1 catalyst. The $H_2O:CO_2$ ratio was 1:2.4. However, with the 1:3 kieselguhr catalyst, we succeeded in reducing the CO_2 content to the extent that approximately equal amounts of CO-oxygen went to CO_2 and H_2O. Further increases in kieselguhr resulted in still less active catalysts; these have not been investigated thoroughly.

Another factor that favors water formation is operation of the kieselguhr catalyst at lower temperatures. With larger quantities of catalyst and a catalyst reactor of larger diameter a sufficient degree of conversion could be obtained at lower reaction temperatures. We used 16 grams of catalyst of composition 1(Fe-Cu-MnO) + 1 kieselguhr. The catalyst was precipitated with soda and taken into operation at 235°C.; then gradually the temperature was lowered to 200°C. Thus we obtained the conditions reported in table 77.

Table 76.—Gas conversion (mixed gas) on kieselguhr-rich Fe-Cu-MnO catalysts

	1 Fe-Cu-MnO 3:0.75:0.75[a] kieselguhr	2 Fe-Cu-MnO 8:2:2 [b] kieselguhr
Temperature, °C.	235	235
Space velocity, liters per hour	3.0	4.1
Contraction, percent	22.0	17.7
CO conversion, percent to CO_2	16.8	12.2
Unchanged CO	52.7	52.1
Synthesis (difference)	30.5	35.7
O_2 conversion, percent to CO_2	33.6	24.4
O_2 conversion, percent to H_2O (difference)	13.7	23.5
$H_2O:CO_2$	1:2.4	1:1.04

[a] The ratio of Fe-Cu-MnO:kieselguhr is 1:2.
[b] The ratio of Fe-Cu-MnO:kieselguhr is 1:3.

Table 77.—Gas conversion (mixed gas) on 1Fe-Cu-MnO (16:4:4) + 1 kieselguhr at 215°-200°C.

	1	2	3
Temperature, °C.	215	205	200
Space velocity, liters per hour	4.2	4.3	2.2
Contraction, percent	29	25.4	27
CO conversion, percent to CO_2	17.8	10.8	14.5
Unchanged CO	47.7	61.0	50.7
Synthesis (difference)	34.5	28.2	34.8
O_2 conversion, percent to CO_2	35.6	21.6	29.0
O_2 conversion, percent to H_2O (difference)	16.7	17.4	20.3
$H_2O:CO_2$	1:2.1	1:1.2	1:1.4
Reaction gas, volume percent:			
CO_2	8.0	5.0	7.0
Olefins	.9	.6	.8
O_2	.0	.0	.0
CO	19.3	23.4	20.6
H_2	58.9	58.8	58.8
Hydrocarbons	1.8	1.0	n.b.[a]
Carbon number	3.3	2.3	n.b.[a]
N_2	11.1	11.2	n.b.[a]
$CO:H_2$	1:3.2	1:2.5	1:2.8

[a] n.b. = not determined.

Table 77 shows that at 215° to 205°C., better results were obtained. For experiment 1, approximately twice as much CO went to synthesis products as to CO_2. For experiment 2, almost three times more was used up for synthesis products than was converted into CO_2. The ratio of $H_2O:O_2$ to the $CO_2:O_2$ lies somewhere between 1:2 and 1:1.2. However, at these low temperatures only 40 to 50 percent of the total CO entered the reaction. Recycling the end gas could be a means of utilizing more of the CO, as the $CO:H_2$ ratio in the reaction gas did not change considerably. For the experiments discussed, this ratio lies between 1:3 and 1:2.5.

The kieselguhr catalysts differ essentially from the non-supported catalysts in that they can form water at low reaction temperatures and are capable of converting a greater portion of the CO to synthesis products. For the non-supported catalysts (see tables 66 and 67), we found that the water formation decreased as the reaction temperatures decreased. As the reaction temperature dropped, water formation finally ceased. For lower temperatures, therefore, the CO_2 value became more and more pronounced when compared to the synthesis value.

"Three-Layer Experiment" with Iron-Kieselguhr Catalysts

Previous experiments showed that the CO present in mixed gas was incompletely converted when kieselguhr catalysts were used. The magnitude of conversion varied between 40 and 70 percent. This lower degree of conversion may result from the dilution of the catalyst when kieselguhr was present; hence, for a certain quantity of catalyst less iron was available. In a further series of experiments we have attempted to increase the gas conversion in one single stage by simply using greater quantities of catalyst, using longer catalyst layers (longer reaction tubes). The reaction tubes used were up to 80 centimeters long. The catalyst tubes used normally were only 30 centimeters in length.

It is interesting to note that an increase in CO conversion in favor of the synthesis products was not obtained in these experiments. It was found that the CO was used up to a greater extent; however, the extra CO was converted to CO_2. At the same time, water formation decreased sharply. These phenomena were observed irrespective of whether the catalyst had the same composition over the entire catalyst layer length or whether the catalyst contained a larger or smaller amount of iron at various places in the reaction tube.

In the following an experiment is discussed in which three catalyst layers were used in series, each catalyst layer being richer in iron than the previous one. Table 78 gives information on the arrangement of the experiment. The total quantity of iron was 14 grams. The first layer was composed of a catalyst with the composition of 1 part of metal to 3 of kieselguhr; the second layer, 1 part of metal to 1 of kieselguhr; and the last layer, no kieselguhr. It may be seen that the catalyst was arranged according to the countercurrent principle. The mixed gas entering was intended to contact the iron-deficient catalyst first, and then proceed to the iron-rich catalyst layers.

Layer 1 was taken into operation at 235°C. until the contraction was 13 percent. Table 78 shows that at this point approximately 35 percent of the CO was converted, and the ratio of the CO which went to CO_2 and synthesis products was equal to 1:1.8, respectively. The $CO:H_2$ ratio shifted only moderately. It was 1:2.4 for the product gas. At this point, catalyst layer 2 was taken into operation. The second layer was contained in an open glass tube of somewhat smaller diameter than the catalyst tube. After a total of 47 hours, the contraction had increased to 29 percent. A total of 75 percent of the CO was converted. The ratio of the CO which went to CO_2 to the CO which went to synthesis products had shifted to 1:1.3; hence the conversion became more unfavorable. The oxygen conversion also had shifted in the direction of an increased CO_2 formation. The $H_2O:CO_2$ ratio was now 1:6.4, and the $CO:H_2$ ratio in the reaction gas had increased to 1:5.1. When the temperature was lowered to 225°C., the CO conversion decreased to 26 percent. The other conversion data shifted in the manner indicated in table 76. When the temperature of 235°C. was reached again, catalyst layer 3 was taken into operation. This caused a decrease of contraction to 25 percent, and conversion conditions prevailed which were similar to those when carrier-free catalysts were used. No water was formed. The $CO:H_2$ ratio in the end gas shifted sharply toward H_2 (1:7.2).

This experiment showed that it was not possible to use more CO for production of synthesis products by employing a longer catalyst bed in connection with kieselguhr catalysts. The reason for this was that the water formed on the succeeding catalyst layers entered into reaction with CO to form CO_2.

In order to re-use the CO when working with kieselguhr catalysts, we found that it was necessary to work in several stages. The water had to be removed between successive stages. We carried out an experiment using tonsil as a carrier. The experiment was not successful, however.

Table 76.—Three-layer experiment

	35 cm.	25 cm.		20 cm.
	Fe-Cu-MnO 2:0.5:0.5 a/ kieselguhr	Fe-Cu-MnO 4:1:1 b/ kieselguhr		Fe-Cu-MnO + 0.1% 8:2:2 K_2CO_3
Temperature, °C.	235	235	225	235
Space velocity, liters per hour	4.1	4.3	3.9	4.1
Contraction, percent	13.0	29.0	26.2	25.4
Hours of operation	23	47	53	73.75
CO conversion, percent to CO_2	12.3	32.4	22.7	40.2
Unchanged CO	65.2	25.1	42.2	19.4
Synthesis (difference)	22.5	42.5	35.1	40.9
CO_2:synthesis products	1:1.8	1:1.3	1:1.5	1:1
O_2 conversion, percent to CO_2	24.6	64.0	45.4	80.4
O_2 conversion, percent to H_2O (diff.)	10.2	10.1	12.4	.2
$H_2O:CO_2$	1:2.4	1:6.4	1:3.7	1:(400)
Reaction gas, volume percent:				
CO_2	5.5	14.8	10.3	17.2
Olefins	.9	.7	.8	.6
O_2	.0	.1	.1	.0
CO	23.2	10.5	17.1	7.7
H_2	55.7	54.1	54.5	55.9
Hydrocarbons	2.9	6.2	3.8	5.6
Carbon number	1.59	1.86	2.01	1.98
N_2	11.8	13.6	14.4	13.0
$CO:H_2$	1:2.4	1:5.1	1:3.2	1:7.2
	Layer 1	Layer 1 & 2	Same at a 10° lower temperature	Layers 1, 2 and 3

a/ The ratio of Fe-Cu-MnO:kieselguhr is 1:3.

b/ The ratio of Fe-Cu-MnO:kieselguhr is 1:1.

Experiments with Tonsil as Carrier

It was interesting to study the influence of the addition of tonsil upon the activity of the iron catalysts and on the course of the reaction. The mode of adding the tonsil was important. In table 79 results are described with a number of Fe-Cu catalysts containing different amounts of tonsil. They were precipitated by soda from ferrous and copper chloride solutions. Experiments 1 and 2 show the effect of the tonsil when mixed in the dry state with an alkalized catalyst and with a nonalkalized catalyst. The catalyst contained Fe and Cu in the ratio 5:1. To this, 4 grams of tonsil were added for every 10 grams of iron. The activity as compared to the tonsil-free catalysts was approximately 25 to 30 percent lower. Otherwise, the course of the reaction was the same; that is, the reaction proceeded by way of CO_2 formation. When the tonsil was added before precipitation, an inactive catalyst resulted (experiments 3 and 4). The alkalized catalyst was even less active than the nonalkalized catalyst. Reduction with H_2 at 450°C. did not change the situation. When the same quantity of tonsil was added after the iron-copper precipitation has taken place, a decrease in activity resulted, but not as much as when the tonsil was added before precipitation. Both catalysts, with and without alkali, reached a maximum contraction of 16 percent and in this condition furnished 26 and 22 grams, respectively, of liquid products per cubic meter of mixed gas. Water was formed simultaneously. Up to 20 grams per cubic meter of gaseous products were obtained. A tonsil-free catalyst, under the same conditions of operation, yielded no water at a contraction of 16 percent. It is evident, therefore, that for the tonsil-containing catalysts, the reaction proceeds partly by way of the formation of water, just as was the case with kieselguhr catalysts. CO_2 formation was suppressed and consequently more CO was available for the formation of hydrocarbons. This is apparent by comparing the end-gas analyses for tonsil-containing and tonsil-free catalysts at approximately the same contraction (table 80). The tonsil-containing catalysts for the same contraction form only half the CO_2 quantity. Correspondingly, the CO content in the end gas is higher than in the case of the tonsil-free catalysts. Normally, using carrier-free iron catalysts, for each mole of CO used up for hydrocarbon synthesis 1 mole of CO_2 should be formed. In experiment 5, we found that a total of 35 percent of CO was used up. Of this, 12 percent went to CO_2 and 23 percent to hydrocarbons. Consequently, for each mole of CO available for the synthesis, only 1/2 mole of CO went to CO_2, or in other words, for this experiment the reaction proceeded to one-half by way of the formation of water and the other, CO_2.

Next we tried to obtain higher conversion by raising the reaction temperature. However, increasing the temperature by 15°C. (from 235° to 250°C.) increased the contraction only to 20 percent. The CO_2 content, however, rose from 4.9 to 8.6 percent, and water formation ceased almost entirely. We are forced to assume, therefore, that at higher temperatures the primary water reacts with the secondary CO to form CO_2. By decreasing the flow velocity from 4 to 1 liter per hour (experiments 5 and 6, table 79), a significantly higher conversion was obtained. We observed that the contraction increased from 16 to 32 percent and 29 percent, respectively. The water formation, however, decreased considerably; whereas the CO_2 content increased to 17 percent. The course of the reaction, therefore, was the same as for the normal iron catalysts. The decrease of flow velocity caused a higher formation of gaseous hydrocarbons, so that the yield of liquid products amounted only to 36 and 35 grams, respectively, although 85 percent of the CO was converted.

Table 79.- Influence of tonsil addition to 5Fe-1Cu catalyst

Experiment No.	K_2CO_3 content, percent	Tonsil quantity, grams	Mode of addition	Reduction conditions	Maximum contraction, percent	Maximum yield, percent	Remarks
1	1/4	4	Mixed in dry after precipitation	Mixed gas immediately	24 235°	41	Decrease of activity by tonsil.
2	Without	4	Mixed in dry after precipitation	Mixed gas immediately	16 235°	17	
3	1/4	4	Tonsil added before precipitation	Mixed gas immediately, H_2, 450°	3 235° 2 235°	- -	By adding tonsil before precipitation, the catalyst was almost entirely inactive.
4	Without	4	Tonsil added before precipitation	Mixed gas immediately H_2, 450°	5 235° 7 235°	- -	
5	1/4	4	Tonsil added after precipitation	Mixed gas immediately	16 4 l./hr. 32 1 l./hr.	26 36	After 6 days, still 16% contraction. Water formation 7 days, later contraction still 27 percent.
6	Without	4	Tonsil added after precipitation	Mixed gas immediately	16 4 l./hr. 29 1 l./hr.	22 35	Still 13% contraction after 6 days. Water formation 7 days, later contraction still 26%.
	Without	4	Tonsil added after precipitation	H_2, 450°	16 235°	-	Behaved like catalyst in experiment 6.
8	1/4	10	Tonsil added after precipitation	Mixed gas immediately	14 250°	-	Increase of tonsil quantity causes more rapid decrease in activity.
9	Without	10	Tonsil added after precipitation	Mixed gas immediately	11 250°	-	

Table 80.--Influence of tonsil upon end-gas composition

Catalyst 5Fe-1Cu	Contraction, percent	End-gas composition							
		CO_2	Olefins	O_2	CO	H_2	Hydrocarbons	Carbon No.	N_2
Contains tonsil + 1/4 percent K_2CO_3	15.5	4.9	0.4	0.2	24.8	57.8	2.1	1.76	9.8
Contains tonsil + 1/4 percent K_2CO_3	16.0	5.4	.6	.1	23.0	58.9	2.1	2.0	9.9
Contains tonsil without K_2CO_3	16.0	5.2	.6	.1	23.3	58.9	2.6	1.85	9.9
Without tonsil, 1/4 percent K_2CO_3	15.5	9.9	.9	.1	17.1	59.6	1.7	1.4	10.7
Without tonsil, 1/4 percent K_2CO_3	15.0	9.0	.4	.1	17.6	60.6	1.5	1.67	10.8

Therefore, it is apparent that neither by raising the temperature nor by decreasing the flow velocity can the reaction be shifted as desired. We tried multi-stage operation in series, which was generally recognized as favoring water formation. The experiment temperature was 235°C. and the flow velocity 4 liters per hour. The end gas of the first stage after the liquid reaction products were removed was recirculated. In this manner, 90 percent of the CO was worked up in four stages. The total contraction was 40 percent (see table 81), and the total of all the liquid hydrocarbons formed in all stages was 48 grams. One can see, therefore, that in comparison to a one-stage operation for the same CO conversion, the formation of gaseous hydrocarbons is favored. This is also evident from the comparatively high content of gaseous hydrocarbons in the end gas. It should be remembered that part of the gas is removed by the activated charcoal after each stage. A CO balance gives the following picture: Of the total CO converted (90 percent) 40 percent went to CO_2 and 60 percent to hydrocarbons. The ratio of CO_2 to hydrocarbons was, therefore, 2:3. From the quantity of CO that was used for the synthesis, theoretically 100 grams of liquid products could be obtained. Since actually only 48 grams of liquid products was obtained, the portion of the CO which was converted to gaseous hydrocarbons was 50 percent.

NOTE. Decreased space velocity causes increased formation of higher molecular weight hydrocarbons.

Table 81.--Four-stage experiment with tonsil-containing catalyst

Stage	Contraction, percent	Grams of liquid products per cubic meter of mixed gas	Gas composition							
			CO_2	Olefins	O_2	CO	H_2	Hydrocarbons	Carbon No.	N_2
1	13.5	22	5.1	0.4	0.3	23.4	58.0	1.8	2.3	11.0
2	10.5	14	10.5	.3	.3	17.1	56.0	4.0	1.88	11.8
3	10.0	8	15.6	.0	.0	9.8	55.4	5.8	1.76	13.4
4	6.3	4	19.5	.1	.3	5.2	54.9	6.0	1.83	14.0
1-4	40.3	48								

In conclusion, we should like to speculate on why we believe that carrier catalysts are capable of forming water and why non-supported catalysts are incapable of doing so. Obviously, with iron catalysts the formation of water is the primary reaction just as it is with cobalt and nickel catalysts. With the carrier-free iron-metal catalysts, this phenomenon of primary water formation is not noticeable because the water formed reacts with part of the CO according to the water-gas equation. The CO_2 once formed is, as was pointed out in the section on "Reduction of the CO_2 on Iron Catalysts", not reduced on the iron catalyst at the temperature range in question. With the carrier catalysts, however, according to observations from the experiments, the subsequent CO conversion by the reaction water takes place only to some extent. It may be that the reason for this behavior is that the catalyst is diluted and that the temperatures at the various active centers are not quite as high as they are with metal catalysts. The metal catalysts, on account of their concentrated form, develop more heat per unit volume, whereas the carrier catalysts develop less heat.

BEST CATALYST OBTAINED

Of the iron catalysts described in the sections on "Iron-Copper Three-Component Catalysts Prepared from Ferric Compounds" and "Needle Iron-Ore Catalysts" the best catalyst found, especially with respect to stability, was a 5Fe-1Cu containing 1/8 percent K_2CO_3. Its method of preparation was as follows: 180 grams of $FeCl_2 \cdot 4H_2O$ (50 grams of Fe) and 26 grams of $CuCl_2 \cdot 2H_2O$ (10 grams of copper) were dissolved in 1 liter of water. The chloride solution was heated to the boiling point and precipitated with a solution containing 160 grams of sodium carbonate in 1-1/2 liters of water (time for precipitation, 1/2 to 1 minute). The precipitate was filtered and washed six times with 1 liter of hot water each time. After drying at 105°C., the catalyst mass was powdered and impregnated with 67-1/2 milligrams of K_2CO_3 (1/8 percent referred to iron). The K_2CO_3 was dissolved in 100 cubic centimeters of water. The impregnated mass was heated with a small flame on the sand bath. It is also permissible to mix the K_2CO_3 solution immediately after the washing operation into the still moist catalyst mass.

A catalyst mass which contained 10 grams of iron was taken into operation without pretreatment. The gas used was mixed gas ($1CO{:}2H_2$), and the flow velocity was 4 liters per hour at a temperature of 235°C. The maximum contraction of 31 percent was reached after 2 days of operation. After the temperature was lowered to 228°C., a yield of 56 grams of liquid products (uncorrected) per cubic meter of mixed gas was found. The average yield for 6 weeks of operation amounted to 52 grams per cubic meter of mixed gas. For 7 weeks of operation, it was 50 grams per cubic meter of mixed gas, and for 8 weeks, it was 47 grams per cubic meter of mixed gas.

From table 82 the behavior of such a catalyst may be observed for 8 weeks of uninterrupted operation. The reaction temperature was raised approximately 10° for a time of operation of 7 weeks. From the gradually decreasing ratio of yield:contraction, one recognizes that the formation of gaseous hydrocarbons increases at the expense of the liquid hydrocarbons. After the seventh week of operation, the reaction temperature was lowered from 237° to 230°C. By doing this, the contraction decreased from 25 to 15 percent. The yield amounted to only 25 grams. The ratio of yield:contraction had increased from 1.52 to 1.66.

Table 82.—Efficiency of a 5Fe-1Cu catalyst + 1/8 percent K_2CO_3 prepared by precipitating $FeCl_2$ and $CuCl_2$ with soda

	Time of operation, days							
	7	14	21	28	35	42	49	56
Temperature, °C.	230	228	229	230	233	233	237	230
Contraction, percent	30	30	30	30	28	26	25	15
Yield of mixed gas, grams per cubic meter	56	55	56	52	47	45	38	25
Average yield of mixed gas, grams per cubic meter	56	56	56	55	53	52	50	47
Yield:contraction	1.87	1.84	1.87	1.73	1.68	1.72	1.52	1.66

In some cases catalysts were obtained by the above-mentioned method of preparation, which gave a maximum yield of 60 grams of liquid products per cubic meter of mixed gas.

REGENERATION OF IRON CATALYSTS

With regard to the possibility of regeneration, the iron catalysts are much easier to handle than the cobalt and nickel catalysts. Whereas, for the cobalt catalyst, a complete reworking of the catalyst is necessary to obtain the original activity (dissolving the catalyst in nitric acid and reprecipitation); iron catalysts may be regenerated simply by treating them with air at the synthesis temperature. Extraction with benzine is recommended first in order to recover the high boiling accumulated paraffin hydrocarbons which are always present in the catalyst.

Regeneration of Fe-Cu Catalysts

Table 83 shows the course of the second operation when using a 5Fe-1Cu catalyst containing 1/4 percent K_2CO_3 which was regenerated under various conditions. These catalysts furnished, during the first operation period, a maximum yield of 56 grams, and after 6 weeks, they still produced 39 grams per cubic meter of mixed gas (average yield for 6 weeks' operation, 49 grams uncorrected). Catalyst 1 was treated first with H_2 at 235°C., then extracted with synthetic benzine (boiling point, 80° to 100°C.), and finally oxidized with air. Catalyst 2 was extracted with benzine and then oxidized with air, whereas catalyst 3 was merely oxidized with air.

Table 83.—5Fe-1Cu catalyst + 1/4 percent K_2CO_3 regeneration under various conditions

Mode of regeneration	Extracted paraffin, grams	Yields, grams per cubic meter after days				
		6	17	24	32	39
1. H_2 treatment at 235°C., benzine extraction, then treatment with air at 235°C.	7.2	55	53	50	43	37
2. Benzine extraction, then treatment with air at 235°C.	9.0	53	50	48	44	35
			after	28	36	43 days
3. Treatment with air at 235°C. only.	-	55	52	49	48	43

For all three catalysts, after regeneration under varying conditions, practically the original maximum yields could be obtained again. Catalyst 3 is even superior to both the other catalysts insofar as stability is concerned. Whereas for catalysts 1 and 2, after removal of the paraffin, a 24-hour oxidation with air was sufficient, unextracted catalyst 3 still consumed part of the oxygen so that it was treated with air for another 48 hours. The reason for the better stability of catalyst 3 seems to be, therefore, the complete removal of the last traces of the high molecular weight paraffins and acids.

It should be mentioned here that a 5Fe-1Cu catalyst containing 1/4 percent K_2CO_3 and formed with starch as a binder reached its original activity after paraffin extraction with benzine and subsequent oxidation with air. The shape of the catalyst had not suffered any during the reactivation. Even after a second oxidation, the shape of the catalyst was still the same. No reactivation was possible by merely conducting H_2 or H_2-NH_3 mixtures over the iron catalysts. When the catalyst was treated with H_2-NH_3 mixtures, a small degree of reactivation was obtained; it was, however, of short duration.

The 5Fe-1Cu catalysts that contained only 1/8 percent K_2CO_3 could be extracted with benzine and subsequently oxidized in a stream of air and thus regain their activity completely. When the catalysts contained only 1/16 percent K_2CO_3, after regeneration, an initial yield of 51 grams was obtained; however, the stability was somewhat impaired and was not quite as good as during the first period (53 grams during first period). Similar observations could also be made with a catalyst activated with Na_2CO_3. However, it seemed that the time of induction for these catalysts, after regeneration, was somewhat longer than for the first period of operation. For this reason too, an activation of Fe-Cu catalysts with Na_2CO_3 instead of K_2CO_3 is not recommended. Extraction alone without subsequent oxidation only causes incomplete regeneration. Other processes of regeneration, such as treatment with steam or heating in a stream of N_2 at 250°C., were without effect.

Regeneration of Cu-Free Catalysts

Regeneration by simple air treatment did not prove successful with the Cu-free catalysts.

The catalysts which were prepared by dissolving iron shavings in dilute nitric acid and subsequent precipitation with Na_2CO_3, containing 1/4 or 1/2 percent K_2CO_3 alkali (they gave a maximum yield of 45 grams and 47 grams of liquid products, respectively) after being treated with air after 8 days of operation gave only a contraction of 13 and 3.6 percent, respectively. During the first 2 days of operation, these catalysts had already given a contraction of 20 and 23 percent, respectively.

REGENERATION OF EXIT GASES

In the section on "Course of Reaction with Iron Catalysts", we have mentioned a difficulty which occurs when the benzine synthesis is carried out on iron catalysts by using mixed gas of composition $1CO+2H_2$. The disadvantage cited is that approximately equal quantities of CO are used up for the formation of hydrocarbons and for CO_2. This conversion to CO_2 is responsible to a great degree for the small yield of approximately 60 grams of liquid products per cubic meter of mixed gas. The degree of liquefaction, by which we mean the percentage of liquid hydrocarbons formed during the synthesis for a certain quantity of CO reacted, is just as good as in the case of the cobalt catalysts, namely 60 to 65 percent. A further increase of the degree of liquefaction at the expense of the small quantities of gaseous products formed appears hardly possible, as a by-product of the reaction CO_2 rather than water is formed.* In some cases, it appears advisable to reconvert the exit gas obtained during the benzine synthesis into synthesis gas. This is to be recommended, since by using iron catalysts, approximately 700 liters of end gas are obtained from each cubic meter of synthesis gas. The average contraction is approximately 30 percent. For this reason we carried out a few experiments on the recovery and regeneration of the exit gases. (*Reasoning here is not clear.)

Use of Coke at High Temperature

The exit gas was conducted at 1000°C. over a layer of granular coke of pea size 10 centimeters in length, contained in a porcelain tube of 16 millimeters inside diameter. To protect the reaction gas from changes which might occur in regions of lower temperature, it was conducted away from the hot zone as rapidly as possible by using a 2-millimeter wide porcelain capillary. The porcelain tube was heated in a Mars furnace.

In table 84 the composition of the product gases is tabulated for various regeneration temperatures.

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Table [illegible].—Conversion of reaction gas on coke at high temperatures

Temperature, °C.	CO_2	Olefins	O_2	CO	H_2	Hydrocarbons	Carbon No.	N_2	Expansion, percent
Final gas from the benzine synthesis	20.5	0.5	0.0	4.0	60.5	3.2	1.2	11.7	—
At 1,030°	2.7	.2	.0	31.0	53.7	2.0	1.0	10.0	10
At 1,100°	1.8	.2	.0	33.4	53.9	.7	1.0	10.0	19
At 1,150°	.6	.1	.0	34.8	54.7	.5	1.0	9.3	23

A synthesis gas is obtained which contains more CO than corresponds to the composition $1CO-2H_2$.

Proof that the carbon participated in the reaction was furnished by the gas expansion during the conversion. This expansion amounted to 23 percent at 1,150°C. From 700 liters of exit gas, therefore, 870 liters of new synthesis gas were regenerated. The carbon used up during the reaction could be accounted for by differences in weight.

Use of Coke at High Temperature in the Presence of Illuminating Gas

In order to arrive at a CO-leaner and H_2-richer synthesis gas, various quantities of city gas were mixed with the exit gas obtained from the benzine synthesis. The mixture thus obtained was conducted over coke at 1,100°C. Table 85 shows experimental results of this regeneration.

Table 85.—Conversion of reaction gas on coke in the presence of city gas at 1,100°C.

Added quantity of illuminating gas, percent	CO_2	Olefins	O_2	CO	H_2	Hydro-carbons	Carbon No.	N_2
15.5	1.2	0.0	0.1	32.4	55.9	1.6	1.0	8.8
18.0	1.0	.0	.0	31.6	57.1	1.6	1.0	8.7
20.5	.7	.0	.0	31.4	57.6	1.3	1.0	9.0
23.0	.5	.1	.2	30.8	57.6	1.2	1.0	9.6
26.0	.9	.0	.1	29.3	58.3	1.6	1.0	9.8
28.5	.8	.0	.2	28.6	59.1	1.6	1.0	9.7
Composition of exit gas from benzine synthesis	21.8	.1	.0	4.4	58.6	3.2	1.13	11.9

With the addition of 26 to 28.5 percent of illuminating gas to the exit gas obtained from the benzine synthesis (the composition of the exit gas as obtained from the synthesis is given in the last column) a synthesis gas is obtained which contains CO and H_2 in the ratio of 1:2. This is not the situation for all exit gases obtained from iron catalysts. For example, we found that for a CO_2-leaner end gas containing only 19 percent CO_2 and 61.8 percent H_2, the addition of 18 percent illuminating gas was sufficient to arrive at a synthesis gas containing 28.3 percent CO and 58.4 percent H_2. The gas expansion observed in this conversion (the conversion of end gas to synthesis gas) amounted to 17-20 percent.

Use of Coke at High Temperatures in the Presence of Broken Clay

A third possibility for regenerating the exit gas obtained from the benzine synthesis consists in heating the gas to very high temperatures in the presence of ceramic material. Table 86 summarizes the reaction-gas analysis after the end gas was conducted over broken clay at various temperatures.

Table 86.—Conversion of reaction gas on broken clay.

Temperature, °C.	CO_2	Olefins	O_2	CO	H_2	Hydrocarbons	Carbon No.	N_2
Composition of the exit gas from the benzine synthesis	17.8	1.0	0.1	5.2	62.3	2.6	1.31	11.0
1,000°	9.6	.0	.0	18.1	57.9	3.0	1.0	11.2
1,100°	4.7	.0	.3	23.9	56.6	2.9	1.0	11.7
1,200°	2.5	.0	.1	26.6	57.3	2.2	1.0	11.3
1,230°	1.8	.0	.3	27.2	57.6	1.9	1.0	11.5
1,300°	1.6	.0	.0	28.1	58.4	.8	1.0	11.1

As is apparent from the table, a reaction temperature of 1,200°C. is required to produce a synthesis gas containing 2.5 percent CO_2, 26.6 percent CO, and 57.3 percent H_2. In accordance with the equation $CO_2 + H_2 = CO + H_2O$, the conversion is associated with a contraction in gas volume, which to a certain extent is compensated by expansion reactions of the hydrocarbons. In the best instance, a maximum contraction of 8 percent was obtained.

This mode of regeneration of the exit gas has the advantage that no new sulfur compounds are introduced into the synthesis gas and, consequently, no additional sulfur purification is necessary.

TWO-STAGE EXPERIMENTS WITH WATER GAS AND MIXED GAS ON IRON-COPPER CATALYSTS, (Meyer)

Water-Gas Experiment

As pointed out in section on "Best Catalyst Obtained", a catalyst composed of 5Fe-1Cu containing 1/4 percent K_2CO_3 (precipitated from $FeCl_2$ and $CuCl_2$ by Na_2CO_3) will give 50 grams of liquid products per cubic meter of mixed gas when permitted to act on a mixed gas of composition 29 percent CO plus 58 percent H_2. This was the case for 6 weeks of operation during which time no regeneration of the catalyst was required. Since, during this experiment, the synthesis gas was depleted in CO and since only moderate quantities of gaseous hydrocarbons were formed, we felt that no considerable increase in yield could be expected in a one-stage operation by merely changing the experimental conditions. We therefore employed water gas instead of mixed gas, in two stages, using iron catalysts of the same composition in both stages. To start with, we attempted to find the highest possible yield and the stability of the iron catalyst. The result of this investigations is given in Table 87.

Table 87.—Maximum yields and stability of Fe-1Cu catalyst containing 1/4 percent K_2CO_3 when water gas was used.

Operation, days	Experiment temperature, °C.	Contraction, percent	Yield in grams of liquid products/m^3 of water gas
6	256	40	75
10	237	35	67
14	237	29	53

After an initial maximum yield of 75 grams per cubic meter, the effectiveness of the catalyst decreased rapidly, as compared with the operation with mixed gas. After 14 days of operation, the quantity of liquid hydrocarbons formed had decreased to 53 grams per cubic meter. Aside from the actual decrease in yield, the deterioration of the catalyst was apparent from the early appearance of yellow reaction products. Yellow products appeared much later when mixed gas was employed. With mixed gas, we could operate for 4 to 5 weeks before the colored product was noticeable. Here again, the catalyst lost activity at approximately the same rate at which yellow products, which we believe to be paraffin decomposition products, were formed. It is plausible to assume that the iron catalyst should exhibit a longer lifetime when only part of the CO in the water gas was converted. For this reason we operated in two stages. Two tubes, each containing 10 grams of iron, operated in series, were charged with water gas at a flow rate of 4 liters per hour. The temperature was chosen so that the contraction after the first stage was 28 to 30 percent. After the gases had passed the first stage, the liquid reaction products were removed and the end gas passed over the second catalyst without removal of the CO_2. The results of this experiment are summarized in Table 88. The sum of the hydrocarbons formed in the first and second stages amounted to a maximum of 85 grams; after 12 days of operation, this was 80 grams; and after 18 days, only 70 grams of total liquid products. In spite of the higher yields, the decrease in activity was not quite as pronounced as when water gas was used in a one-stage operation. However, during a two-stage experiment, twice the catalyst quantity was used.

Table 88.—Two-stage experiment with water gas on a 5Fe-1Cu catalyst containing 1/4 percent K_2CO_3.

		First stage		Second stage		
Operation, days	Temp., °C.	Contraction, percent	Liquid products, $g./m^3$	Contraction, percent	Liquid products, $g./m^3$	Sum of liquid products collected in first and second stages
7	230	30	55	20	30	85
12	232	27	52	18	28	80
18	230	20	42	18	27	70

We believed that increasing the flow velocity from 4 to 8 liters per hour, corresponding to twice the catalyst quantity, would yield poor results with the two-stage experiment. However, we have not carried out this experiment, because, even with a flow velocity of 4 liters per hour, the yield had already decreased from 55 grams to 42 grams in the first stage after only 18 days of operation. Since the load on the catalyst for the first stage of the operation was no larger than that of a one-stage operation operating with mixed gas (because here also for the same contraction of 30 percent, the same yield was observed, and in addition, for a considerably longer time of operation), the faster decrease in activity in the first stage when using water gas should be attributed to the higher concentration of CO in the water gas. If the flow velocity should be doubled, this effect would become even more pronounced, than with a corresponding increase in flow velocity when mixed gas is used. In the latter case, the maximum yield is 51 grams with a flow velocity of 8 liters per hour (60 grams at 4 liters per hour); and after 10 days of operation, it decreased to 46 grams.

With respect to the stability of the iron catalysts, we consider it undesirable for the reasons mentioned above to employ them with water gas.

Mixed Gas Experiments.

Without Regeneration of End Gas After the First Stage.

Two-stage experiments with mixed gas in which the end gas was passed over a second iron catalyst after the gasoline had been removed appeared not very promising to us. The reason is that the CO is already converted rather completely after one single stage. Gaseous products appear only in small quantities. In fact, when we did carry out a two-stage experiment in which the space velocity was doubled, namely 8 liters per hour, corresponding to twice the catalyst quantity, no improvement in the yield of liquid hydrocarbons was observed.

With Regeneration of End Gas After the First Stage.

We were interested in finding out what kind of yields per cubic meter of mixed gas could be obtained when the end gas was scrubbed free of the benzine and then passed over pieces of clay at 1,200°C. This operation regenerated the gas and converted it to synthesis gas. It was passed over an iron catalyst again. The arrangement of the experiment was as follows: The first stage was charged with 3(Fe-Cu catalyst) containing 1/8 percent K_2CO_3. The flow velocity was 12 liters of mixed gas per hour. The product gas scrubbed free of liquid reaction products and continuously regenerated on pieces of clay in a Mars furnace at 1,200°C. The synthesis gas thus formed was immediately conducted into the second stage. The second stage was only charged with 2 parts of iron catalyst as the gas volume was reduced from 12 to 8 liters per hour after passage through the Mars furnace. Table 89/contain the results of this experiment.
and 90

~~Table 89.~~—Two-stage experiment with mixed gas and regeneration of end gas from the first stage.

	Temp., °C.	Contraction, percent	Liquid products, grams per cubic meter of mixed gas
First stage	230	30	56
Second stage	230	26	37
First and second stage	-	Approximately 50% referred to starting gas.	93

Table 90.—Composition of starting gas and reaction gas for both stages

	CO_2	Olefins	O_2	CO	H_2	Hydrocarbons	Carbon No.	N_2	Residual gas quantities still present from 1,000 liters
Starting gas, first stage.	1.0	0.0	0.0	29.6	59.5	1.8	1.0	8.1	1,000
End gas, first stage	19.9	.1	.3	3.9	59.9	5.6	1.21	11.2	700
Regenerated end gas	2.4	.0	.2	26.3	56.9	3.0	1.0	11.2	680
End gas, second stage	19.8	.9	.2	2.5	58.6	4.9	1.5	14.9	500

It is possible, therefore, to obtain from 1 cubic meter of mixed gas, 93 grams of liquid products, of which 56 were obtained in the first stage, and 37 in the second stage. However, gas regeneration was necessary after the first stage. Referring the yield to normal conditions, the value increased from 93 to 102 grams per cubic meter of mixed gas. From the last column of Table 90, it is obvious that from 1,000 liters of mixed gas, 500 liters were still present leaving the second stage. After another regeneration of this end gas, 25 grams of additional liquid hydrocarbons could be obtained; so with a three-stage operation, a yield of 127 grams per cubic meter of mixed gas should be anticipated.

Nothing definite can be said about the economic feasibility of such a process. Perhaps the synthesis end gas should be passed through the generator during the gas production period. A two-stage operation with water gas in which the end gas is regenerated after the first stage, gave a higher yield for the first days of operation than mixed gas. The yield with water gas amounted to 70 grams for the first stage, and 33 grams for the second, a total of 103 grams (uncorrected). The activity of the iron catalyst, however, decreased more rapidly with water gas, especially in the second stage. The reason is that the end gas contained more CO than H_2 after it was regenerated at 1,200°C. For example, its CO content was 44 percent and H_2 content only 32 percent.

Two-stage Experiment with Water Gas

First stage: Fe catalyst. Second stage: Co catalyst.

Finally, we want to report the results of a two-stage experiment in which the first stage was operated with an iron catalyst, and the second stage with a cobalt catalyst. As a starting gas, we used water gas. It was our intention to convert enough CO during the first stage so that the end gas had approximately the composition $1CO + 2H_2$. A gas of such a composition is desirable for the operation of the gasoline synthesis on cobalt catalysts. In this manner, gasoline could be easily obtained in places where local conditions provide sufficiently cheap water gas. The results of such an experiment are summarized in Tables 91 and 92. Gasoline and oil were removed after the first stage. The CO_2 formed was not scrubbed out.

Table 91.--Two-stage experiment with water gas
(First stage, Fe catalyst) 10 grams Fe.
(Second stage, Co + 18 percent ThO_2) 4 grams Co.

Stage	Temp., °C.	Contraction, percent	Liquid products, g./m³
First stage (Fe)	224	21	35
Second stage (Co)	180	64	68
First and second stages			103
First stage (Fe)	228	27	47
Second stage (Co)	180	57	68
First and second stages			115

Table 92.—Composition of reaction gas after the various stages.

	CO_2	Olefins	O_2	CO	H_2	Hydrocarbons	Carbon No.	N_2
End gas, first stage	14.7	0.5	0.0	28.5	46.6	1.2	1.75	8.5
End gas, second stage	35.7	1.7	.1	25.6	13.9	6.0	1.74	17.0
End gas, first stage	20.1	1.1	.1	23.3	44.2	2.2	1.77	8.9
End gas, second stage	46.4	1.5	.3	8.9	15.2	10.3	1.82	17.4

The first row in Table 91 indicates that the first stage gave 35 grams of liquid products at a contraction of 21 percent (iron catalyst). The end gas analysis (Table 92) shows, however, that the gas composition $1CO+2H_2$ was not reached and that CO was still present in excess. With this end gas, a yield of 68 grams was obtained in the second stage using cobalt catalyst. The contraction was 64 percent (Table 91, row 2). In both stages together, therefore, 103 grams per cubic meter of water gas (uncorrected) were formed. The end gas analysis of the second stage indicates plainly than an excess CO was present as far as the cobalt catalyst was concerned. During a second experiment, therefore, we charged the iron catalyst stage somewhat more heavily. With a contraction of 27 percent (row 3), the yield amounted to 47 grams and the end gas corresponded approximately to a $1CO+2H_2$. This end gas furnished 68 grams of liquid products per cubic meter of water gas in the cobalt stage (row 4). Consequently, a total of 115 grams per cubic meter of water gas were formed. The end gas leaving the second stage still contained CO and H_2 in approximately the ratio of 1:2, which indicates that the gas used for charging the second stage corresponded to the usage ratio of CO and H_2. If one expresses the residual CO and H_2, in percent, taking into consideration the contraction which had occurred, one finds that only 5.7 percent CO and 9 percent H_2 did not enter into the reaction. 14.5 Percent CO was utilized to form gaseous hydrocarbons. A certain quantity of CO_2 (corresponding to the quantity of hydrocarbons formed) appeared at the end of the first stage. During the second stage, no additional CO_2 formed. The CO_2 obtained in the first stage was apparently not attacked in the second stage; the CO_2 quantity after the second stage was equal to that after the first stage. Furthermore, if the CO_2 had been partly hydrogenated, the H_2 balance should have given an indication of that; the gaseous hydrocarbons formed should be composed of molecules incorporating fewer carbon numbers. The question of CO reduction with iron catalysts will be discussed in detail later. It is apparent from the experiments that with mixed gas advantages result in a multistage operation only when the end gas, after each stage, is regenerated by thermal treatment.

The execution of such an experiment with water gas is not recommended on account of the rapid decrease of activity of the iron catalysts, especially after the second stage. Water gas, however, can be used successfully in a two-stage operation without regeneration if the first stage is charged with an iron catalyst, and the second stage with a cobalt catalyst. A more frequent regeneration of the iron catalysts becomes necessary, however.

SIGNIFICANCE OF IRON CATALYSTS FOR THE SIMULTANEOUS PRODUCTION OF CO-DEFICIENT CITY GAS AND GASOLINE IN CONNECTION WITH GAS WORKS. (Meyer)

Considering the byproduct, coke, obtained from the illuminating-gas industry, it would be desirable for many gas works to use part of the coke for production of a standard city gas and simultaneously gasoline. For this purpose, the water gas produced should be processed first to remove the CO_2 formed.

From the H_2-rich synthesis gas thus produced, containing, for example, 20 parts of CO and 70 parts of H_2, with cobalt catalysts under proper reaction conditions, approximately 50 grams per cubic meter of liquid products can be obtained. The end gas from the synthesis, which is lean in CO, conforms closely to the specifications of a standard city gas.

The further possibility of the production of standard city gas, practically free of CO, and the simultaneous production of gasoline on cobalt catalysts will not ~~be discussed~~ further. We want to discuss the possibility of perhaps producing a standard city gas when iron catalysts are used during the synthesis.

Table 93.—End gas with Fe catalysts for gases of various CO contents.

Temp., °C.	Operation, days	Contraction, percent	Liquid products per cubic meter of gas, grams	End gas composition							
				CO_2	Olefins	O_2	CO	H_2	Hydrocarbons	Carbon No.	N_2
			1a Synthesis gas: $20CO-75H_2$								
226	-	27	47	10.2	0.5	0.0	1.8	80.5	2.1	1.67	4.2
After removal of CO_2				—	.6	.0	2.0	90.4	2.3	1.67	4.7
			1b Synthesis gas: $29CO-58H_2$								
230	20	30	52	19.3	1.4	0.0	4.0	60.1	4.4	1.68	10.8
After removal of CO_2				—	1.7	.0	5.0	74.4	5.5	1.68	13.4
230	15	31	56	19.7	0.9	.0	3.5	61.3	4.3	1.63	10.3
After removal of CO_2				—	1.1	.0	4.4	76.6	5.4	1.63	12.5

Table 93 gives some end gas analyses which were obtained when various starting gases were used with 5Fe-1Cu catalysts containing 1/4 percent K_2CO_3 (precipitated from $FeCl_2$, $CuCl_2$, and sodium carbonate). The experimental conditions were such that optimum yield of liquid hydrocarbons were produced. By using an H_2-rich synthesis gas of composition 20 percent CO and 75 percent H_2, which is also especially suitable for the production of a proper city gas when cobalt catalysts are used, iron catalysts produce an end-gas which after removal of the CO_2 contains approximately 90 percent H_2 and only small quantities of hydrocarbons (Experiment 1a). With mixed gas ($29CO-58H_2$) and under conditions favorable for the benzine synthesis, an exit gas is obtained during Experiment 1b, as indicated. By raising the experiment temperature from 230° to 245° C. temporarily, twice the quantity of gaseous hydrocarbons may be obtained (as may be seen by comparing experiment 1 with 2 in Table 94.

Table 94.—End gases with Fe catalysts and mixed gas at elevated temperatures.

Gas[1]	Temp., °C.	Operation, days	Contraction, percent	Grams of liquid products, m³. gas	End gas composition							
					CO_2	Olefins	O_2	CO	H_2	Hydrocarbons	Carbon No.	N_2
a	230	6	30	53	19.3	0.5	0.2	3.4	61.8	3.3	1.5	11.5
b					—	.6	.3	4.2	76.5	4.1	1.5	14.3
a	245	7	33	—	20.0	1.5	.3	1.7	57.5	6.4	1.5	12.6
b					—	1.9	.4	2.1	71.9	8.0	1.5	15.7
a	245	11	28	—	19.2	1.2	.3	4.0	59.1	4.4	1.4	11.8
b					—	1.5	.4	5.0	73.1	5.4	1.4	14.6
a	270	12	34	—	20.2	1.9	.4	1.8	56.0	7.0	1.27	12.7
b					—	2.4	.5	2.3	70.0	8.8	1.27	16.0
a	270	14	26	—	17.2	1.4	.2	4.8	60.0	5.1	1.25	11.3
b					—	1.7	.2	5.8	72.5	6.2	1.23	13.6
a	300	14	34	—	19.2	2.3	.0	3.5	54.5	8.1	1.26	12.4
b					—	2.8	.0	4.3	67.5	10.0	1.26	15.4
a	300	15	11.5	—	9.7	.9	.2	17.4	59.1	3.1	1.07	9.6
b					—	1.0	.2	19.3	65.5	3.4	1.07	10.6

[1] a = 29CO - 58H_2. b = after removal of CO_2.

On account of the higher experiment temperatures, the activity of the catalyst decreased rapidly with the simultaneous formation of yellowish products. After 4 days of operation, starting from the increase in temperature to 245°C., the contraction decreased from 33 to 28 percent. The end gas had a composition as shown in row 3. The quantity of the gaseous hydrocarbons formed, therefore, decreased and was approximately of the same order of magnitude as that from an iron catalyst operated at 230°C. A further increase in the reaction temperature to 270°C., caused a rise in contraction and in formation of gaseous hydrocarbons (column 4). It is apparent from the low carbon numbers that primarily CH_4 was formed. After two further days of operation, the contraction decreased from 34 to 26 percent. Correspondingly, the quantity of gaseous hydrocarbons decreased (column 5). We also carried out an experiment at 300°C. Referred to CO_2-free gas, initially 10 percent of gaseous hydrocarbons were formed. After 24 hours, the contraction decreased to 11.5 persent, and only 3.4 percent of saturated gaseous hydrocarbons were observed.

Table 95.—End gases with Fe catalysts and water gas.

Water gas[1]	Temp., °C.	Operation, days	Contraction, percent	Grams of liquid products, m³ gas	End gas composition							
					CO_2	Olefins	O_2	CO	H_2	Hydrocarbons	Carbon No.	N_2
a	236	6	40	75	36.1	2.3	0.2	6.1	41.5	4.2	1.88	9.6
b					—	3.6	.3	9.5	65.0	6.6	1.88	15.0
a	236	10	36	67	30.5	2.8	.3	11.0	40.8	4.8	1.6	9.8
b					—	4.0	.4	15.8	58.8	6.9	1.6	14.1

[1] a = 44CO - 47H_2. b = After removal of CO_2.

Table 95 reports the composition of two end gases obtained with water gas on an iron catalyst. An increase of the gaseous hydrocarbons as compared to the mixed gas experiments had not taken place. Experiments at elevated temperatures were not carried out, because iron catalysts lose activity more quickly when water gas is employed than when mixed gas is used even in low-temperature regions. An increase in temperature therefore, and the use of water gas with iron catalysts would certainly tend to decrease the lifetime of the iron catalysts still more than in the case of mixed gas.

In summation, it can be said that the reaction gases obtained from the benzine synthesis when using iron catalysts did not possess the proper requirements of a good city gas. The concentration of gaseous hydrocarbons in the exit gas was too low, and the required heating value thus was not assured. The different composition of the end gases obtained with iron catalysts as compared to cobalt catalysts may be explained by the different course of the reaction on iron and cobalt. Since, on account of CO_2 formation, only half of the CO in the synthesis gas was converted into hydrocarbons when iron was used, the amount of gaseous hydrocarbons in the exit gas was considerably lower than when cobalt was used. Furthermore, with cobalt catalysts, a considerable increase in gaseous hydrocarbon content occurred on account of the high contraction caused by water formation. This was not the case with iron catalysts because chiefly CO_2 was formed, which did not reduce the contraction as much as the condensable water. By scrubbing out the CO_2, this disadvantage could be overcome to a certain extent. The H_2 usage with iron catalysts was small. Consequently, after the CO_2 had been scrubbed out of the end gas, the remaining gas contained approximately 60 to 65 percent H_2, when water gas was the original gas. With mixed gas, a final end gas containing 70 to 75 percent H_2 was obtained after the CO_2 had been scrubbed out; and with a starting gas consisting of 20 percent CO and 75 percent H_2, an end gas resulted containing 90 percent H_2. For this reason, the end gas had too small a density and did not correspond to city gas requirements.

An increase in experiment temperature is not to be recommended in connection with iron catalysts, since the increased yield in gaseous hydrocarbons did not reach the desired degree and the life of the iron catalyst was considerably impaired. With the decrease in lifetime of the catalyst, the amount of gaseous hydrocarbons formed decreased as well.

It was thought that a small addition of nickel or cobalt to the iron catalyst should favor the formation of gaseous hydrocarbons, and thereby increase the heating value of the end gas. For this reason, we added 1 and 5 percent nickel and cobalt, respectively, to a 5Fe-1Cu catalyst. The preparation of the catalyst was carried out by simultaneous precipitation of the three metals. The catalysts were taken into operation with mixed gas at 235°C., in one case directly, and in another case, after an H_2 treatment. All catalysts furnished a final gas which did not differ appreciably from the end gas obtained directly with a 5Fe-1Cu catalyst without nickel or cobalt, as far as the contents of gaseous hydrocarbons was concerned.

With a content of 5 percent nickel, the activity of the catalyst was somewhat inferior to the nickel-free catalyst, whereas with a content of 5 percent cobalt, the activity was not impaired.

REDUCTION OF THE CO_2 ON IRON CATALYSTS (Bahr).

In previous chapters, we referred repeatedly to the high content of CO_2 in the end gas obtained from carrier-free iron catalysts. We have had end gases containing as much as 20 percent or more of CO_2, in addition to a high H_2 content (60 percent). Since it is known that the CO_2 may be reduced at a lower temperature than the CO, this simultaneous appearance of CO_2 and H_2 in the same gas in the presence of the iron catalysts is astonishing. Especially is this true since CO_2 can be reduced with ease at 150°C., when cobalt or nickel catalysts are present. The explanation may be that the iron catalyst in the presence of cobalt and nickel can not reduce CO_2 at low temperatures. Kuester (38) has reported no noticeable reduction of CO_2 to methane at temperatures below 300°C., but only at elevated temperatures, 350°-400°C. However, at temperatures of around 200°C., a reduction of CO_2 to CO occurs.

The kieselguhr catalysts which form some reaction water do not behave differently as far as the CO_2 reduction is concerned. Of the experiments mentioned, let us consider the following in greater detail: An Fe-Cu-MnO (4:1:1) kieselguhr (1:1) catalyst was used. Starting at 150°C. with a gas containing 14.8 percent CO_2 and 83.4 percent H_2, the temperature had to be raised to 200°C. before a small contraction of 3 percent could be measured. At 275°C., a contraction of 6 percent was observed; at 350°C. (4 liters of throughput per hour), 19 percent contraction was noticed. At this temperature, the reaction gas in addition to 10.7 percent residual CO_2, also contained 3.3 percent CO and 2.1 percent paraffin hydrocarbons. The latter had a carbon number of 1.9; hence, the observation by Kuester was confirmed, that the CO_2 is not only converted to methane in the presence of iron catalysts, but also to higher hydrocarbons. At 400°C., the contraction increased only a small amount, and eventually reached 21 percent. In addition to 10.4 percent residual CO_2, the product gas also contained 4.7 percent CO and 3.2 percent paraffin hydrocarbons with a carbon number of 1.37. In the cold section of the reaction tube, a small amount of yellow oily products condensed. Calculation showed that the CO_2 (on 100 percent basis) was converted in the following manner by the catalyst at 350° to 400°C.

	Percent		
Temp., °C.	Unchanged CO_2	To CO	To paraffin hydrocarbons
350	58.8	18.2	21.8
400	35.4	25.0	23.0

At 400°C., a small analytical error was introduced into the determination, as the sum total of the unconverted and converted CO_2 is more than 100 percent.

The result of these experiments may be summarized by saying that even with the iron catalysts which are capable of forming some reaction water, reduction of the CO_2 was not observed at the reaction temperatures of the benzine synthesis. Thus may be explained the fact that in the reaction gases obtained from iron catalysts, appreciable quantities of H_2 can coexist in these gases with fairly large quantities of CO_2.

COPPER-FREE IRON CATALYSTS (Meyer)

Finally, we want to report on the results which we obtained with copper-free iron catalysts. With reference to earlier experiments, we want to refer to the "Gesammelten Abhandlungen zur Kenntnis der Kohle" (vol. 10). Of special interest are the results obtained with iron-aluminum and iron-silicon alloy catalysts (39). In contrast to the nickel- and cobalt-skeleton alloy catalysts, iron-aluminum and iron-silicon alloys, after removal of the aluminum with NaOH, were almost entirely inactive. An improvement did not result even when the catalysts were oxidized.

That it is possible to obtain comparatively good yields of liquid hydrocarbons with iron alone (without copper) may be seen from the following investigations.

Preliminary Experiments.

To ascertain what the catalytic activity of a pure ferrous iron catalyst is, greatest care was taken that during the preparation of such a catalyst oxidation to the ferric condition was avoided.

In the beginning, we used $NaHCO_3$ as precipitant since the precipitations obtained with $NaCO_3$ or K_2CO_3 had a tendency to discolor very rapidly and change from green or black into brown. The precipitation with $NaHCO_3$ seemed more stable. The preparation of ferrous carbonate from $FeSO_4$ and $NaHCO_3$ was accomplished by adding the hot solution of $FeSO_4$ to a solution of $NaHCO_3$ under constant stirring. In order to assure complete precipitation, heating was continued for some time on the water bath under a CO_2 atmosphere. The grayish-white precipitate was then filtered in the presence of CO_2 and washed free of sulfates with boiling water. The drying of the $FeCO_3$ was accomplished in a vacuum at room temperature. The catalytic activity of this catalyst was very slight (2.5 percent contraction at 245°C.), and an increase could not be obtained by a preliminary reduction with H_2 at 400°C. In order to exclude the possibility that the activity of the catalyst was reduced by residual sulfate sulfur, ferrous nitrate was used as starting material for the preparation of $FeCO_3$. For this purpose, iron shavings were dissolved in dilute nitric acid of a specific gravity 1.035. Solution was carried out in the cold, the precipitation of the ferrous nitrate being accomplished with $NaHCO_3$ in the manner already described. With this catalyst, a contraction of 4 percent was obtained during 8 days of operation.

As an alternative method for the preparation of $FeCO_3$, we resorted to the precipitation of ferrous formate by means of $NaHCO_3$. Ferrous formate was obtained by dissolving iron shavings in dilute formic acid, and processed as described above. With this $FeCO_3$ and an experiment temperature of 242°C., a maximum contraction of 26 percent was obtained. However, it should be mentioned that it took 10 days of operation to reach this contraction. The maximum yield of liquid hydrocarbons was 42 grams per cubic meter of mixed gas. When the experiment temperature was raised with another batch of $FeCO_3$, produced in the same way, a maximum contraction of only 5 percent could be obtained. It is, therefore, apparent that the activity of the $FeCO_3$ catalyst, prepared according to this method, is not reproducible. The precipitation of ferrous formate with $NaHCO_3$ in presence of kieselguhr led to catalysts which were inactive. A catalyst prepared by precipitating ferrous sulfate with soda exhibited no activity either. However, a $FeCO_3$ catalyst prepared from ferrous formate and Na_2CO_3 gave a maximum contraction of 12 percent. The results with the copper-free ferrous carbonate catalysts so far investigated are tabulated in Table 96.

Table 96.—Activity of ferrous carbonate prepared in various manners.

Exp. No.	Mode of preparation	Carrier	Pretreatment	Temp., °C.	Maximum contraction, percent	Maximum yields of liquid products, g./m³ mixed gas
1	$FeSO_4$ + $NaHCO_3$	Without	Mixed gas immediately	245	2.3	-
2	$FeSO_4$ + $NaHCO_3$	Without	H_2 400°	245	2.0	-
3	$Fe(NO_3)_2$ and $NaHCO_3$	Without	Mixed gas immediately	238	4.0	-
4	Ferrous formate and $NaHCO_3$	Without	Mixed gas immediately	242	26.0	42
5	Same as 4, (retest)	"	"	242	5.0	-
6	Ferrous formate and $NaHCO_3$	Kghr.	Mixed gas immediately	245	3.0	-
7	$FeSO_4$ and Na_2CO_3	Without	Mixed gas immediately	242	.0	-
8	Ferrous formate and Na_2CO_3	Without	Mixed gas immediately	242	12.0	-

In the section, "Iron-/ Copper Catalysts from Ferrous Compounds", 5Fe-1Cu catalysts were described in detail, which were prepared by precipitating the chloride from hot solution with Na_2CO_3. These catalysts were alkalized with 1/4 percent K_2CO_3, and after approximately 6 weeks of operation, they gave an average yield of 50 grams of liquid products per cubic meter of mixed gas. Table 97 contains the results which were obtained with a similarly prepared catalyst which was copper-free, however, and contained various quantities of K_2CO_3.

Table 97.—Iron alone, prepared/$FeCl_2$ by precipitation with Na_2CO_3; various quantities of K_2CO_3 in catalyst.

Exp. No.	Catalyst composition	K_2CO_3 content, percent	Contraction, percent after days 7	14	21	Yield, grams per cubic meter of mixed gas	Remarks
1	Iron alone	0	12	12	15	22	After 3 weeks, no further increase in activity.
2	do.	1/8	14	17	20	33	do.
3	do.	1/4	18	17	23	30	do.
4	do.	1/2	13	18	20	25	do.

The influence of the K_2CO_3 addition was not as pronounced as in the case of the copper-containing catalysts. This, of course, refers only to the catalysts prepared from $FeCl_2$. With other modes of preparation, as will be shown in a later chapter, a subsequent addition of K_2CO_3 can cause a considerable increase in activity. The catalysts precipitated from $FeCl_2$ and containing various quantities of K_2CO_3 require a long period of induction just as do the K_2CO_3-free catalysts. The maximum contraction for these catalysts is reached only approximately after 3 weeks of operation, and the yields obtained up to this time do not show any great differences. The K_2CO_3-free catalyst furnished 22 grams; with the catalyst containing 1/8 percent K_2CO_3, 33 grams; 1/4 percent K_2CO_3, 30 grams; and 1/2 percent K_2CO_3, 25 grams of liquid products per cubic meter of mixed gas were obtained. The experiment temperature in all cases was 240°C. Consequently, it was approximately 10° higher than for the corresponding copper-containing catalysts. After 3 weeks of operation, no further increase in activity was observed.

Principal Experiment (Ackermann).

Dumped Weight* and Mode of Preparation.

In spite of the very voluminous and varied research on catalysts, no information has been obtained so far from which one could predict just how active a certain catalyst would be. In all cases, it was necessary to carry out a time-consuming activity determination. The reasons for this are well-known. With the precipitated catalysts, it was found that the mode of precipitation produces important differences in the dumped weight of the catalyst. The determination of the dumped weight of the catalyst may be carried out very quickly. Therefore, we attempted to find the possible relationship between dumped weight of a catalyst, and its activity. It was pointed out that chemical changes might occur in the iron catalysts during the synthesis which would not have any connection with the dumped weight of the catalyst, and also, that the catalytically active portion of the catalyst surface does not have a simple relationship to the degree of dispersion as indicated by the dumped weight.

Precipitation. The aqueous solutions of ferrous chloride and ferric nitrate were precipitated with aqueous solutions of sodium carbonate, potassium carbonate, and sodium hydroxide and potassium hydroxide. The conditions, such as concentration, temperature, and addition of reactants, varied in all cases. The precipitant was always dissolved in a quantity of water which was to 3/4 the volume of the iron salt solution. It was always used in 10 percent excess. After filtering, the precipitant was washed 6 times with water. The water used for each washing was equal to 10 times the weight of the iron which was to be washed. The catalysts were dried for 20 hours and 110°C., and were then ground into a fine powder. Thereafter, the dumped weight was determined by shaking the catalyst in a graduated cylinder until no more reduction in volume occurred upon further shaking. From the dumped volume and the weight of the catalyst, the dumped weight was calculated.

Precipitations with soda. As may be seen from Tables 98 and 99, the dumped weights vary between 0.28 percent and 1.00 percent. There seems to be a fundamental difference in the dumped weights of the pre-

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*The term "dumped weight" as used in this and the succeeding pages in this section is defined as bulk density at maximum packing.

cipitated ferrous catalysts and the precipitated ferric catalysts. The explanation may be that from ferrous salts, at first, ferrous carbonate is precipitated, whereas from ferric salts, ferric oxyhydrate is formed. This at first voluminous and very difficultly filterable precipitate bakes on drying and forms a blackish-blue brittle mass. It has an especially high dumped weight.

From ferrous salts, at first, a white ferrous carbonate precipitates out which forms an easily filterable dense crystalline precipitate. Decomposition sets in as soon as the washing operation is begun, and as soon as the air has access to it. The precipitate is gray at first and then changes to black. (After a longer period of contact with the air, the black mass changes into a reddish-brown ferric hydroxide.) When dried at 110°C., the main quantity of the CO_2 is driven from the ferrous carbonate, causing a very pronounced loosening of the mass. This loosening is the more pronounced the denser (larger crystals) the original ferrous carbonate. Those precipitates which were most easily filtered had the smallest dumped weights after drying.

The greatest variation between dumped weights and precipitating conditions occurred with the normal precipitation of the ferrous chloride* (Table 98, precipitation 5 to 10.).

Table 98.—Dumped weight with normal precipitation of ferrous sulfate, ferrous chloride, and ferric nitrate with sodium carbonate.

Iron salt	Exp. No.	Concentration, grams of iron per liter of solution	Temp., °C.	Dumped weight, percent
Ferrous sulfate	1	50	20	0.35
	2	50	100	.43
	3	10	20	.50
	4	10	100	.42
Ferrous chloride	5	100	20	.50
	6	100	100	.56
	7	50	20	.43
	8	50	100	.31
	9	10	20	.58
	10	10	100	.51
Ferric nitrate	11	50	20	1.00
	12	50	100	.83
	13	10	20	.83
	14	10	100	.87

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* Normal precipitation - addition of precipitant to iron salt solution.
Reverse precipitation - addition of iron salt solution to precipitant.

Increase of the temperature (100°C.) as well as increase in concentration caused a noticeable reduction in the dumped weight. With reversed precipitation (Table 99), however, small dumped weights were only obtained when chloride ions were added to the soda solution in advance in the form of NaCl (Table 99, Experiments 21 and 22). This observation may be explained by assuming that in the presence of chloride ions, the seeding of the crystals proceeds slowly. At the same time, the velocity of crystal growth of the $FeCO_3$ crystals increases. Whereas in the case of the normal precipitations sufficient chloride ions are already present in the precipitation mixture from the very beginning, in the case of reverse precipitation chloride ions have to be added to the sodium carbonate solution before the precipitation is carried out.

Table 99.—Dumped weight with reverse precipitation of ferrous sulfate, ferrous chloride, and ferric nitrate with sodium carbonate

Iron salt	Exp. No.	Concentration, grams of iron per liter of solution	Temp., °C.	Dumped weight, percent	Remarks
Ferrous sulfate	15	50	20	0.39	
	16	50	100	.39	
	17	10	20	.48	
	18	10	100	.48	
Ferrous chloride	19	50	20	.37	
	20	50	100	.43	
	21	50	100	.32	10 grams of NaCl to 10 grams of iron
	22	50	100	.28	20 grams of NaCl to 10 grams of iron
	23	10	20	.50	
	24	10	100	.59	
Ferric nitrate	25	50	20	.83	
	26	50	100	.87	
	27	10	20	.74	

Precipitations with potassium carbonate. The same observations were made when the corresponding precipitations were carried out with K_2CO_3. Here we succeeded, for instance, with the reverse precipitation of 50 grams of iron per liter of ferrous chloride at 100°C., in reducing the dumped weight from 0.46 to 0.25 by the addition of KCl to the K_2CO_3 solution. The dumped weights of the precipitations of the three iron salts with potassium carbonate, in general, were in good agreement with those obtained by precipitating with sodium carbonate solutions. Consequently, it is not necessary to recite these values.

Precipitations with sodium hydroxide. The precipitations with sodium hydroxide gave, in all cases, high dumped weights. The results of these precipitations did not depend on whether ferrous or ferric salts were used. The dumped weights obtained varied from 0.6 to 0.9. It is a known fact that from ferrous salts, at first, a white ferrous hydroxide is precipitated, which is very difficult to filter in the presence of ferrous carbonate. Upon drying, it did not loosen up. On account of the ease with which it could be oxidized after the drying operation, it consisted chiefly of ferric oxide. The dumped weights of all the catalysts which were produced as ferric oxide fragments or "slates" depend somewhat on the size of the powder after being pulverized;

powdered by means of a mortar:

10 minutes	15 minutes	20 minutes
0.74	0.61	0.59

Catalytic Investigations of Catalysts with Various Dumped Weights.

We employ the contraction as a measure of the activity of the catalyst. An equivalent of 10 grams of iron was used with 4 liters per hour of mixed gas at 240° to 250°C. Table 100 contains the various catalysts arranged according to their increasing dumped weight. Considering catalysts that were precipitated from the same salt, no relationship seems to exist between contraction and dumped weight. The comparison of catalysts prepared from different salts, however, shows that the ferric nitrate catalysts are more active than the ferrous chloride catalysts: Activity increases with increased dumped weights and decreases with small dumped weights.

Table 100.—Dumped weights and catalytic activity of sodium carbonate-precipitated ferrous chloride and ferric nitrate catalysts (nonalkalized).

Iron salt	Catalyst No.	Dumped weight, percent	Maximum contraction, percent	Temp., °C.	Operation, hours
Ferrous chloride	1	0.26	8	250	120
	2	.30	4.5	250	46
	3	.42	8.5	240	64
	4	.43	14	250	46
Ferric nitrate	5	.83	22	240	90
	6	.83	21	240	90
	7	.87	23	240	90
	8	1.00	26	250	71

This finding contradicts the opinion that catalytic activity increases with decreasing dumped weight. As a matter of fact, the dumped weight does not seem to give any information on the (inner) catalytic active surface of a catalyst. A more appropriate means of testing the catalytic properties would be perhaps determination of the heat of adsorption, which may be readily obtained as the heat of wetting when ethanol is used, for instance. Thus, we found that a catalyst precipitated with sodium carbonate from ferrous chloride and having a dumped weight of 0.31 percent exhibits a heat of wetting of only 2.3 calories per gram of iron, when 96 percent of alcohol was used. The corresponding precipitated ferric nitrate catalyst with the dumped weight of 0.83 percent had a heat of wetting of 9.4 calories per grams of iron. It can be said that dumped-weight determinations are not suited to predict the catalytic properties of iron catalysts, ferrous and ferric. Another reason for this is the fact that the catalysts themselves, under the same washing conditions, contain various amounts of foreign material which has been introduced through the precipitation. Later washing experiments showed that the ferric nitrate catalysts mentioned in Table 100 must have contained considerable amounts of Na_2CO_3. This was probably responsible for the higher activity those catalysts exhibited, when compared to the chloride catalysts.

Table 101.--Dumped weights and catalytic activity of sodium carbonate-precipitated ferric nitrate catalysts, exhaustively washed, in comparison to NH_3- and $(NH_4)_2CO_3$- (respectively) precipitated ferric nitrate catalysts (nonalkalized)

Iron salt	Catalyst No.	Precipitant	Dumped weight, percent	Temp., °C.	Maximum contraction, percent	Operation, hours
Ferric nitrate	1	NH_3	0.98	240	7.5	84
	2	$(NH_4)_2CO_3$	1.00	235	10.0	120
	3	Na_2CO_3	1.00	235	7.5	120
	4	Na_2CO_3	1.00	234	11	120
	5	Na_2CO_3	1.00	234	11.5	120

As Table 101 shows, the activity of thoroughly washed, soda-precipitated catalysts was not higher than the activity of the precipitated ammonia- or ammonium carbonate-precipitated catalysts.

Determination of the Alkali Quantity Needed for Alkalization.

Estimation of alkali quantity according to chlorine content in catalyst. The addition of alkali-carbonate as an activating influence upon the iron one-component catalysts is similar to that on the multicomponent catalysts. To study the effect of the alkali, an experiment was performed in which the alkali was to combine with anions in the catalyst which were believed to be damaging to the catalyst. With this, the function of the alkali would be fulfilled. An excess of alkali in such an instance would be desirable. As the experiment reveals, however (Table 102), this assumption was unjustified because the activity kept on increasing with increasing alkali addition, and it increased independently of the quantity of chloride present, which it was supposed would interact with the alkali.

Table 102.--Influence of alkalization of a catalyst prepared from ferrous chloride with sodium carbonate at 100°C., containing an equivalent amount, twice the equivalent amount, and 10 times the equivalent amount of alkali.

Chloride content: 0.026 percent,
requires 0.051 percent K_2CO_3 for neutralization.

K_2CO_3 percent	Temp., °C.	Contraction, percent	Operation, hours
0	240	6	160
.05	240	10	160
.10	240	15	160
.50	240	17	160

Excess alkalization and removal of unadsorbed alkali quantities by filtration and washing, respectively. During alkalization of catalysts, we generally found that the alkalinity of the slurry formed with the K_2CO_3 solution decreased after a short time. This we believe resulted from adsorption of alkali on the catalyst. In the following experiment, therefore, we permitted the catalyst to take up an optimum alkali quantity. A catalyst precipitated from ferric nitrate with sodium carbonate was impregnated with 0.5 percent K_2CO_3 when still moist. From samples (c) and (d), the alkalization liquor was removed by filtration, and sample (d) was washed twice. Table 103 shows that, with increasing subsequent removal of the K_2CO_3, the activity decreased.

Table 103.—Ferric nitrate-precipitated catalyst alkalization and subsequent removal of alkali by filtration and washing.

Sample	Pretreatment, percent K_2CO_3	Temp., °C.	Activity: Contraction after days of operation, percent 2	4	8	20	58
a	0	232	13.3	19.4	24	26	23.5
b	1/2	232	25	27.5	25	5	—
c	1/2 percent removed by suction.	232.	11.5	15	15.5	21	—
d	1/2 percent removed by suction and washing.	232	11	10	8.6	11	

Aside from finding that possible adsorption of the optimum alkali quantity which might have taken place on the catalyst was not permanent, as could be seen from the fact that with subsequent removal of K_2CO_3 the activity decreased, this experiment gave some other very important information. Titrating with 1/10 N hydrochloric acid the filtrate obtained from the washing operation of sample (d) (methyl red), we found an alkali quantity three times as large as the quantity of K_2CO_3 added for alkalization. The excess alkali can only have originated from the catalyst itself and probably remained there on account of insufficient washing. Hence the catalyst had been prealkalized by the precipitating sodium carbonate. From this observation, the slowly increasing activity of sample (a) may be explained; the course of the activity increase is characteristic for sodium carbonate alkalization. Likewise, the rapid decrease in activity of sample (b) may be due to overalkalization (Na_2CO_3 and 1/2 percent K_2CO_3 present).

Precipitation in presence of fixed alkali. Two catalysts were prepared by precipitating ferrous nitrate and ferric nitrate with ammonium carbonate. The contraction of these catalysts, for example, after 5 days of operation at 235°C., amounted to 7.5 percent for the ferrous nitrate catalyst which was not alkalized, and ~~was 9~~ percent for the same catalyst containing 1/2 percent K_2CO_3. For a nonalkalized ferric nitrate catalyst, the contraction was 9.7 percent and for the ferric nitrate catalyst alkalized with 1/2 percent K_2CO_3, 23.5 percent. As one can see, the activity of the nonalkalized catalysts, which are obviously free from alkali, is very small. Activation with alkali is especially pronounced in the case of the ferric nitrate catalyst.

Exhaustive washing of ferric nitrate catalysts precipitated with sodium carbonate. According to experiments so far with iron one-component catalysts, more active catalysts may be obtained by precipitating ferric nitrate than are obtained by precipitating such ferrous salts as, for instance, ferrous nitrate or ferrous chloride. We have found that the resulting activity is independent of the precipitant. With regard to the precipitant, we found that Na_2CO_3 was superior to $(NH_4)_2CO_3$. According to this, the most active catalyst should be expected to result from a precipitation of ferric nitrate with sodium carbonate. It was our aim to find the optimum quantity of alkali necessary for such a catalyst. During this determination, residual alkali quantities still present in the catalyst (due to more or less thorough washing of the catalyst), were determined by titration with HCl and further washing until worthwhile quantities of sodium carbonate were no longer removed from the catalyst.

In this manner, the most active iron one-component catalyst so far was obtained; when alkalized with 1/2 percent K_2CO_3, it gave a contraction up to 31 percent and yielded 55 grams of liquid hydrocarbons (oil + gasoline) per cubic meter of mixed gas. Following is the mode of preparation of such a catalyst, and the catalytic testing employed in determining its activity.

Most Effective Iron One-Component Catalyst.

Method of preparation (normal experiment). A solution was prepared by dissolving ferric nitrate containing 50 grams of iron in one liter of boiling water*. Into this boiling solution, a boiling solution of 160 grams of sodium carbonate in 750 cc. of water was added as rapidly as CO_2 evolution permitted, stirring constantly. It was brought to a boil for a very short time and filtered hot through a filter funnel. The difficultly filterable precipitate was washed 10 times with 1 liter of water for each washing. Then it was dried in air at 110°C. for 20 hours; the dried and brittle catalyst was powdered in a mortar.

Alkalization and catalytic activity. The moist catalyst was mixed with a solution of the calculated quantity of K_2CO_3 in a little water and dried at 110°C.

From Table 104, it may be seen that, with increasing quantities of alkali, the activity increases. The catalyst containing 1/4 percent K_2CO_3 furnished its maximum contraction after 4 days of operation; when containing 1/8 percent K_2CO_3, it reached a maximum contraction after 10 days; with 1/16 percent after 5 to 6 days; and without alkali, after 3 days. The time of induction, which in every instance was no longer for this catalyst than for an iron-copper catalyst, passed through a maximum with a K_2CO_3 content of 1/8 percent. As will be shown by time tests, catalysts that require a long time for induction are less susceptible to fatigue than catalysts that require a short time for induction. After 14 days of operation, the catalyst with 1/4 percent K_2CO_3 formed yellow products. At the same time, the yield of liquid hydrocarbons had decreased by 8 grams per cubic meter. The nonalkalized catalyst gave a contraction of only 10 percent for the whole time of operation.

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*The ferric nitrate used for this and further experiments was prepared by dissolving technical iron in dilute nitric acid and heating the ferrous nitrate solution with concentrated nitric acid.

Table 104.—Activity determination of a precipitated ferric nitrate catalyst (precipitated with sodium carbonate) which was exhaustively washed. Influence of quantity of K_2CO_3; operating temperature, 233°-235°C.

Operation, days	0 percent K_2CO_3		1/16 percent K_2CO_3		1/8 percent K_2CO_3		1/4 percent K_2CO_3	
	Contraction, percent	Liquid products $g./m^3$	Contraction, percent	Liquid products $g./m^3$	Contraction, percent	Liquid products $g./m^3$	Contraction, percent	Liquid products $g./m^3$
1	8.8	—	13	—	14.6	—	18	-
3	10.4	—	15.5	—	20.8	—	27.7	-
4	10.4	—	18	—	22	—	29.5	-
5	11	11.2	19.6	33.1	24.5	42.5	29.8	55
7	9.6	12.2	22.5	31.3	23	44.1	30.0	54
10	—	—	22.0	38.4	26.5	46.6	28.7	53
14	—	—	20.7	38.1	26.3	45.8	28	47

Catalytic activity during life tests. The experimental results in Table 105 are to be judged as follows: 1/4 percent K_2CO_3: Time of induction, 3 to 4 days; more than 50 grams of liquid hydrocarbons up to the tenth day of operation; 50 to 40 grams up to the 22d; and 40 to 30 grams up to the 38th day of operation. 1/8 percent K_2CO_3: Time of induction, 8 days; more than 40 grams of liquid products up to the 38th day of operation. The average yield between the 3d and 238th day of operation for the catalyst containing 1/4 percent alkali was 43 grams; for the catalyst with 1/8 percent alkali, it was 44 grams of liquid hydrocarbons. The addition of 1/8 percent K_2CO_3 produces as good an average yield for 38 days of operation as the addition of 1/4 percent K_2CO_3. Possibly the optimum alkali quantity is somewhere between 1/8 and 1/4 percent.

Table 105.—Behavior of sodium carbonate-precipitated ferric nitrate catalysts exhaustively washed and in operation for a longer period.

Operating temperature: 233°-235°C.

Operation, days	Catalyst No. 1		Catalyst No. 2		Canalyst No. 3[1]	
	Contraction, percent	Liquid products, $g./m^3$	Contraction, percent	Liquid products, $g./m^3$	Contraction, percent	Liquid products, $g./m^3$
1	14	—	15.8	—	15	—
3	24.5	—	29.3	—	29.3	—
5	25.3	43.5	29.5	51.4	31.8	—
7	26	46.2	28.5	51.2	32.0	54.5
10	26.7	50.6	29.0	47.2	31.2	50.0
14	26.0	46.0	27.0	41.0	31.4	—
17	26.0	42.0	26.2	38.1	30.0	48.3
21	26.5	42.3	26.2	37.6	30.0	45.0
24	27.0	44.7	26.5	37.7	28.7	—
26	—	—	—	—	27.5	38.8
28	—	43.2	—	35.5	—	—
31	—	—	—	—	27	37.2
38	26.3	39.9	21.5	28.3	26.0	33.6

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[1] Catalyst 3 was prepared in the same manner as catalyst 2 (fresh precipitation). The above figures show that it was somewhat superior to catalyst 2.

Pelleting and catalytic activity. The catalyst, which was impregnated with 1/4 percent K_2CO_3, was compressed in the pelleting machine (cross-section--mm. thickness, 1 to 2 mm.). The increase of activity was somewhat more rapid than in the case of nonpelleted catalysts. The activity decrease, however, was faster. The maximum contraction was reached after 3 days, with a yield of 54 grams of liquid hydrocarbons. On the 10th day of operation, it had decreased to 50 grams; between the 10th and 14th days, it varied between 50 and 40 grams; and at the end of the 22d day, it was 30 grams of liquid products per cubic meter of gas. After 38 days of operation, only 13 grams of liquid hydrocarbons were formed.

Conversion of CO with water vapor at synthesis temperature. In connection with the gasoline synthesis, we were also interested in finding out whether the iron one-component catalyst can accelerate the water-gas shift at benzine-synthesis temperatures.

A catalyst which contained 1/4 percent K_2CO_3 and was prepared by precipitating from ferric nitrate was allowed to act on mixed gas at 235°C. for 48 hours. The resulting contraction was 24.5 percent. Following this reaction, a mixture of CO with steam, containing both components in the ratio 1:1, was passed over the catalyst. (Two liters of CO were bubbled through water at 83°C.; the vapor pressure of water at this temperature is 1/2 atmosphere.) In the end gas, we found 32 percent CO_2 and only 7.3 H_2, whereas the CO content had decreased by 36.6 percent. The expansion was only 5 percent. (According to the water-gas generation and assuming CO_2 formation, an expansion of 32 percent is expected.) Consequently, we are justified in concluding that the benzine synthesis occurs simultaneously with the water-gas reaction. If one assumes that 1 CO_2 is formed from approximately 2CO + $1H_2$ at conditions of the benzine synthesis, one is in a position to calculate approximately the original water-gas conversion. According to this, about 20 percent of the CO was converted with water. After 24 hours, the CO_2 decreased to 20 percent, whereas the expansion increased simultaneously to 9 percent. We concluded that the benzine synthesis had decreased more rapidly than had the water-gas reaction. At the same time, we found that 1 gram of yellowish oil had collected in the receiver. After switching to mixed-gas, the catalyst at first gave 13 percent contraction; 48 hours later, it gave 28 percent contraction and again produced colorless oil.

We have found that the iron one-component catalyst at synthesis temperatures can shift the water-gas equilibrium toward CO_2 formation. This discovery, however, does not explain why the benzine synthesis takes a different course over the iron one-component catalyst from that over cobalt and nickel catalysts.

Regeneration Experiments.

With H_2 at synthesis temperature. A catalyst which, after 20 days of operation, gave only the small contraction of 27.5 percent and furnished yellow oil was treated with 4 liters per hour of H_2 at 232°C. During the H_2 treatment, the hydrocarbons leaving the catalyst in small quantities did not have a brighter color. When mixed-gas was used again, yellow products formed just as before. The contraction after the H_2 treatment was practically the same as before; however, after 4 days of operation, it decreased to 21 percent. Consequently, no regeneration had occurred.

With superheated steam at synthesis temperature. The experiments with steam may be summarized by saying that the fatigued catalysts were treated with 10 liters per hour of steam at 230°C. The contraction at first decreased to 0 percent and increased slowly again. When the steam was allowed to act on the catalyst for 24 hours and when thereafter mixed gas was admitted again, the original contraction had not been restored. When the catalyst was treated with steam for only 4 hours, the original contraction was obtained with mixed gas after 3 days of operation. In all cases, we observed that the liquid products remained yellow. Consequently, no regeneration had taken place.

Oxidation with air at synthesis temperature. After treating the catalyst for 40 hours with 4 liters per hour of air at 235°C., the contraction decreased from 25 percent to 0 percent. Even when the catalyst was allowed to act on mixed gas for several days, it remained inactive.

The regeneration experiments demonstrated, therefore, that so far we have not succeeded in regenerating an iron one-component catalyst.

Alkalization with Sodium Carbonate

The alkalization with 1/8 percent, 1/4 percent, and 1/2 percent of sodium carbonate yielded a smaller activity than with the corresponding potassium carbonate experiments. The times of induction were longer. After approximately 8 days of operation with 1/4 and 1/2 percent Na_2CO_3, maximum contractions of 23 and 28 percent, respectively, were obtained. The maximum yield for a catalyst containing 1/2 percent Na_2CO_3 was 45 grams of liquid hydrocarbons after 8 days of operation. It is interesting to observe that the catalysts alkalized with potassium carbonate retained their activity for a longer period of time. After 42 days of operation, the catalyst containing 1/2 percent Na_2CO_3, still yielded 40 grams of liquid hydrocarbons; the one containing 1/4 percent Na_2CO_3, after the same length of time, still gave 36 grams of liquid hydrocarbons. For both catalysts, however, the oil was yellowish. At this point we want to mention a catalyst for which we observed the longest time of operation ever obtained for an iron one-component catalyst. This was a ferric nitrate catalyst precipitated with sodium carbonate which was, however, not washed exhaustively. (See table 103, test a). This catalyst was not alkalized after the washing operation; however, the water from the washings showed that at least 1/2 percent Na_2CO_3 was still contained in the catalyst as residual alkali originating from the precipitation. It reached its highest contraction after 20 days of operation (27 to 28 percent; maximum yield, 46 grams), and between the 8th and 42d days of operation gave more than 40 grams of liquid hydrocarbons. On the 58th day of operation, the contraction was still 23.5 percent and the yield 38 grams.

Multicomponent Catalysts Precipitated Like the Best Iron One-component Catalyst.

Iron-copper catalysts. Stimulated by the good results with iron one-component catalysts, it was suggested that we find out what influence the presence of copper would have on the best iron catalyst. It appeared to us that a further increase in activity should not be impossible. As the experiments show, however, no improvement, but rather deterioration resulted. We precipitated ferric nitrate-cupric nitrate solutions in the same manner with sodium carbonate as we precipitated the iron salts from which the pure iron catalyst was made. The copper quantities used were 1 percent, 5 percent, and 20 percent. For the first series of experiments, the catalysts were not alkalized. In the course of 7 days of operation, no effect of the copper could be determined. All three catalysts behaved exactly as did the copper-free iron catalysts; the contraction was around 10 percent at 235°C. In another series of experiments, the catalysts were alkalized with 1/4 percent K_2CO_3. The contraction increased to 27 to 28 percent independently of the copper quantity. The yield of liquid hydrocarbons was, in the best case, 49 grams per cubic meter. After 24 days of operation, the products formed were yellow at an average contraction of 26 percent and 38 grams of yield.

Iron-zinc oxide catalysts. A precipitated ferric nitrate catalyst, after having been alkalized with 1/4 percent K_2CO_3, was mixed with some ground, freshly prepared zinc nitrate. Three catalysts of different zinc contents were thus formed, containing iron and zinc in the ratios 100:1, 10:1, 2:1. The zinc carbonate was precipitated from zinc nitrate with sodium carbonate. When the activity of these catalysts was determined, we found that the catalysts containing 100 parts of iron to 1 part of zinc, and 10 parts of iron to 1 part of zinc acted virtually in the same way as did the zinc-free catalysts. The maximum contraction was 31 to 32 percent; 54 to 50 grams of liquid hydrocarbons per cubic meter of gas were formed.

The catalyst which contained 2Fe-1Zn required a longer period of induction. It gave its maximum contraction after 10 days of operation (30 percent, with 49 grams of liquid products). After 38 days of operation, it showed a somewhat smaller decrease in activity than the more zinc-deficient catalysts. The influence of the zinc, which is present in the form of zinc oxide, at synthesis temperature is therefore only slight.

Ferric Nitrate Decomposition Catalysts.

If we had succeeded in preparing decomposition catalysts which had the same activity as the precipitated catalysts, we could have cheapened the catalyst considerably by saving the sodium carbonate, the wash water, and some time of operation. As starting material, we used ferric nitrate solution. It was evaporated to the consistency of a syrup (partial decomposition). Through some preliminary experiments we found that the catalyst is more active the faster the decomposition occurred. Therefore, the thickened nitrate solution was rapidly decomposed by introducing small portions into an iron pan heated directly. It was stirred continuously until the evolution of nitrous oxide fumes almost ceased. The red-brown oxide was immediately removed from the hot pan. The best catalysts were obtained when alkalization was carried out before the decomposition. The alkalization was accomplished by adding the calculated quantity of potassium carbonate to the nitrate solution. With 1/4 percent K_2CO_3 and at 235°C., a contraction up to 29 percent was reached, and 48 grams of liquid hydrocarbons per cubic meter of mixed gas were formed. It did not matter whether the catalyst was powdered or whether it was used in granules such as were obtained after the decomposition. As compared to the precipitated catalysts, a faster decrease of activity was noticeable; after 13 days of operation, the contraction decreased to 25 percent and the yield to 38 grams per cubic meter.

A treatment with mixed gas followed by air, and vice versa, before taking the catalyst into operation, proved to be less desirable than treatment with mixed gas alone.

We added some starch to the catalyst to be pelleted (1 gram of starch per 10 grams of iron). The pellets had a diameter of 3 mm. Their activity could not be initiated when treated with mixed gas alone. By treating first with air and following with mixed gas, a catalyst which contained 1/2 percent K_2CO_3 gave 14 percent contraction.

REACTION PRODUCTS FROM IRON CATALYSTS

Since the laboratory experiments yielded very small quantities of material, we did not make very thorough analytical studies on the composition of the reaction products. In this connection, we refer to the end of this section where we have discussed the results of a semiplant-scale operation.

Content of Unsaturated Hydrocarbons in Synthesis Products (Gasoline + Oil) as Obtained on Iron Catalysts. (Bahr)

We found that an iron-copper-manganese (4:1:1) catalyst containing 1 percent K_2CO_3 gave the following products containing unsaturated hydrocarbons, as shown in the following table.

	1	2	3	4	5	6
Temperature, °C.	200	210	220	230	240	240
Space velocity, liters per hour.	2.7	4.0	4.4	4.6	3.4	9.8
Volume percent in H_2SO_4 divided by P_2O_5 soluble (unsaturated)	18.2	4.9	18.5	19.4	29.3	41.7

The above summary shows that the content of unsaturated compounds in the reaction products varied bewteen 5 and 42 volume percent. Except for some irregularities, we found that the oil is more unsaturated when it was produced at a higher reaction temperature. Furthermore, we can recognize that at lower gas rates an oil is produced which is more saturated (Experiments 5 and 6). With water gas, a product is obtained which is richer in unsaturated compounds. The gasoline plus oil obtained from water gas at reaction temperatures between 230 and 240°C., for instance, contains 15 percent volume percent unsaturates.

Paraffin Extraction from Iron Catalysts.

In the course of the synthesis, the iron catalyst like the cobalt catalyst takes up a certain quantity of paraffin which it retains within its body. We extracted this paraffin from the catalyst using benzol or hydrogenated Kogasin I. Thus, we obtained up to 30 percent of paraffin, based on the catalyst weight. The quantities of paraffin incorporated in the iron catalysts were not quite as high as in the case of the cobalt catalysts. The reason for this may perhaps be that these NaOH iron catalysts, on account of their short life, did not have enough time to be completely saturated with paraffin.

A closer investigation of the extracted paraffin showed that, just as with the cobalt paraffin, it could be separated into a lower-melting and a higher-melting portion by extraction with a solvent such as ether. By multiextractions, with ether, of the high-melting portion, a product could be obtained that had a solidification point of 99°C. and melted between 114° and 117°C. Consequently, high-melting paraffins may be obtained from the iron synthesis also.

Table 106.—Quantities of paraffin retained by 5Fe-1Cu catalyst; relationship between this quantity of paraffin and K_2CO_3 content of catalyst (10 grams Fe)(Meyer)

Exp. No.	K_2CO_3 content, percent	Operation, days	Consumption of mixed gas per m^3	Extraction of paraffin, grams	Paraffin, g./m^3 of mixed gas	Contraction Percent	Contraction After days
1	0.	50	5.0	4.5	0.9	20	42
2	1/16	60	6.0	6.5	1.1	28	42
3	1/8	60	6.0	7.8	1.3	26	42
4	1/4	55	5.5	10.1	1.8	26	42
5	1/2	20	2.0	10.0	5.0	18	21
						7	32
6	1	10	1.0	12.0	12.0	6	9
7	2	7	.7	8.2	11.7	7	4

Table 106 gives information about the quantities of paraffin contained in iron catalysts with varying amounts of K_2CO_3. These data are for a definite period of operation. The third from the last column indicates the quantity of paraffin (in grams per cubic meter of mixed gas) obtained from the catalyst by extraction with synthetic benzine (fraction 80°-100°C.). The catalyst with 1/4 percent K_2CO_3 contained approximately twice as much paraffin as did the catalyst which contained no K_2CO_3. A catalyst containing 1/2 percent K_2CO_3, after being in operation for 20 days, took up the same quantity of paraffin as did a catalyst containing 1/4 percent K_2CO_3 after 55 days of operation. Still larger paraffin quantities were contained in the catalysts alkalized with 1 percent and 2 percent K_2CO_3. The catalysts lost activity with increasing paraffin formation (last column). It should be noted that the decrease of the activity does not depend on the quantity of the paraffin taken up by the catalyst but rather on the simultaneous appearance of decomposition products of the paraffin. These decomposition products appear in greater concentration when heavily alkalized catalysts are used. For the catalysts containing little K_2CO_3, the decomposition products do not appear as early.

In summary, it can be said that with iron catalysts, up to approximately 12 grams of high-melting paraffins may be extracted from the catalyst per cubic meter of mixed gas, provided the catalyst contains 1 to 2 percent K_2CO_3. To preserve the life of the iron catalyst, it is recommended, therefore, that only small to moderate alkali quantities be added.

Acid Products (Bahr)

Just as in the case of cobalt catalysts, so also with iron, not only gasoline, oil, and paraffins are obtained, but small quantities of acid products also. When the synthesis was carried out with carrier-free catalysts, these acid products were chiefly found in the oil, but also to some extent in the paraffin in the catalyst and could be extracted by boiling with a one to 2 normal Na_2CO_3 or NaOH solution. Yellow extracts were obtained which, after an acidification and extraction with ether, and evaporation of the ether, left behind semiliquid products of pungent odor reminiscent of the higher fatty-acid series. In one case, we obtained 0.5 gram of such acid products after extracting 40.5 grams of a catalyst, that is, approximately 1 percent of the catalyst weight. Perhaps the activating alkali content of the catalyst gradually entered into reaction with the acid products and formed soaps. Possibly, also, fatty-acid salts of iron, copper, and manganese appeared to a lesser degree. In this connection, an older experiment is of interest in which the spent catalyst, after paraffin extraction, was treated with sulfuric acid. When extracted with benzol, the catalyst gave 9 percent paraffin as referred to the catalyst weight. In order to remove some ether-soluble products, which might still be in the catalyst, it was boiled out with ether, and thereafter it refluxed with dilute sulfuric acid. When the acid was added, almost violent CO_2 evolution occurred. After the insolubles were filtered off, the sulfuric acid solution was extracted with ether in a perforated funnel. The insoluble residue from the catalyst was extracted with ether also. Both extractions were combined, the ether evaporated off; the combined residue amounted to 1.2 grams of a liquid product in which small solid particles were dispersed. The whole mass had a pungent odor. Referred to the final weight of the catalyst, approximately 9 percent paraffin and 4.4 percent "acid products" were obtained.

It does not appear that the decreased catalyst activity should be caused by a combination of the acid materials with the alkali of the catalyst (to form fatty-acid salts). As already mentioned, we added 1 percent of potassium acetate to the catalyst without impairing the activity of the catalyst. in the section, "Iron-copper Three-component Catalysts Prepared from Ferric Compounds"

Whether the iron catalysts, on account of the added alkali, have a stronger tendency than cobalt to form acid products could not be ascertained to date.

Strangely enough, the reaction water and the liquid products obtained from the water-forming kieselguhr catalyst react less acid than the liquid products of the carrier-free catalysts. Either the acid products do form to a smaller extent when carrier catalysts are used, or are retained to a greater degree by the carrier catalyst.

ADVANTAGES AND DISADVANTAGES OF IRON CATALYSTS.

The advantages and disadvantages of using iron catalysts may be summarized as follows:

1. When iron catalysts are used, we shall not have to rely on the expensive and rare cobalt, but can use instead, the cheaper iron which is available in Germany in unlimited quantities. The addition of thorium

which is expensive is not required. The iron catalysts can be prepared technically in the same type of apparatus as the cobalt catalyst, that is, either by dissolving iron in nitric acid or hydrochloric acid. Soda may be used for the precipitation in both cases.

2. The iron catalyst may be taken into operation with mixed gas immediately at the proper reaction temperature without previous reduction with H_2 at higher temperatures. For this reason, no reduction furnace (working at higher temperatures) is required as compared, for instance, to the reduction of the copper-free cobalt catalyst, where such a furnace is used.

3. The life of the iron catalysts available up to now may be regarded as sufficiently long.

4. The fatigued iron catalyst may be regenerated by a simple treatment with air, after extraction. By doing so, the catalyst regains its activity. This is in contrast to cobalt catalysts.

5. The highest yield thus far obtained with iron catalysts is 60 grams per cubic meter of mixed gas. The average yield for 6 weeks of operation is 50 grams per cubic meter of mixed gas (uncorrected).

6. The products of the iron catalysts (gasoline, oil, and paraffin) are qualitatively the same as in the case of the cobalt catalysts. The iron catalyst offers the possibility of producing gasolines with a high content of unsaturates.

7. The iron catalyst has the advantage of being cheaper, more easily taken into operation , and requiring simple regeneration. It has the disadvantage, however, over the cobalt catalyst in that it furnishes only half as high a yield.