FILM STUDY GROUP

REPORT ON MICROFILM REEL NO. 101

Prepared by

BUREAU OF MINES

RECENT INVESTIGATIONS ON IRON CATALYSTS

Recent Investigations on Iron Catalysts

Contents

The various investigators are mentioned along with their work in the respective paragraphs.

I. 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 Erdoelsynthese"[1]. In the following, a short resume is given of the state in which this research was at that time.

----

[1] Ges. Abh. Kohle, Bd. 10.

The highest yields obtained with iron catalysts at that time amounted to 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 products were added which were believed to be favorable and increase the activity. At this time, we used sodium-glass powder, and sodium aluminate of composition $1Al(OH)_3 \cdot 1/3NaOH$. The additional products amounted to 10 percent and were mixed in dry form to the finished iron-copper oxide mixture. The mentioned catalysts were tested with water-gas. The time for which the catalysts remained active was not very long. At that time, 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 the following experiments, we used 10 grams of iron most of the time. Hence for the earlier runs, the catalyst quantity 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, a direct comparison between the yields at that time with the yields which are obtained at present is not possible immediately. 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 which was used at that time consisted of $4Fe + 1Cu + 10$ percent sodium aluminate ($1Al(OH)_3 + 1/3 NaOH$). 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 g./m³ 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 the years 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 g./m³ 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 lifetime of this catalyst was very short how-
ever. Already during 20 to 25 hours of operation, the contraction decreased
by 1/3. 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 which was comparable to the calcu-
lated yield.

For the following experiments, chiefly, Fe-Cu-2-component and Fe-Cu-MnO-3-
component catalysts were used. For the experiments which used Fe-Cu, the cata-
lysts were chiefly formed from ferrous compounds. The Fe-Cu-MnO-3-component
catalysts were formed from ferric nitrates exclusively. For the sake of clarity
these two catalyst species are dealt with separately in Sections II and III.
In the course of the experiments, it was found that iron was capable of giving
good results when used alone under certain experimental conditions. These Fe-
1-component experiments are described in Section XV.

II. Iron Copper Catalysts from Ferrous Compounds.

In the following, these results are first described which were obtained with
iron-copper catalysts that were produced by precipitation of various ferrous
compounds under various conditions. The ferrous compounds were made by dis-
solving iron shavings in various acids, in some other cases, the ferrous com-
pounds 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 more
in detail), the same catalysts were investigated containing 20 percent of cop-
per. 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.

    1. Dissolving iron-metal in formic acid and precipitation with sodium
carbonate.

Iron shavings were dissolved in dilute formic acid, and the resulting iron-
formeate solution was precipitated in the cold with sodium bicarbonate and in
the presence of copper nitrate (20 percent of copper). The washing of the
catalyst was carried out in a CO_2 atmosphere in order to avoid an oxidation
of ferrous carbonate to ferric hydroxide. The drying of the catalyst was car-
ried out in vacuum at room temperature. For the investigation of 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 of H_2, was 4
liters per hour. The catalysts were taken into operation without any previous
pretreatment.

Since by the addition of manganese to iron-copper catalysts which were produced
from ferrous compounds, the catalysts could be activated more or less correspond-
ing to the production conditions, we investigated how an alkalization of the
manganese would effect the activity. We found that alkalization of the man-
ganese did not improve the efficiency of the catalyst. For the sake of clear-
ness, we discussed the influence of manganese and some other additions to the
ferrous catalysts at the same place where we discussed the iron-copper catalysts
without additions.

Table 1.

Activity of Copper-Containing Ferrous Catalysts
(From Ferrous Formeate by Precipitation with Sodium Bicarbonate)

Catalyst Composition	Preparation Conditions	Exp. Temp., °C.	Maximum Contraction Percent	Days	Max. yields in g./m³ of mixed gas
5Fe - 1Cu	Ferrous-formeate and copper-nitrate precipitated in the cold with NaHCO₃.	238	25	2	39
5Fe - 1Cu	" " "	235	26	3	40
5Fe - 1Cu + 10% basic MgCO₃	Ferrous-formeate and copper-nitrate precipitated in the cold with NaHCO₃, basic MgCO₃ mixed in dry.	235	27	3	47
5Fe-1Cu-1/4Al	Precipitation with NaHCO₃ (simultaneous)	235	23	5	43
5Fe-1Cu-1Mn	" " " "	237	26	4	48 (?)

Table 1 contains results of some catalysts which were prepared by the mentioned methods. With an iron-copper catalyst containing iron and copper in the ratio of 5:1 (Experiment 1), 39 grams of liquid products were obtained per normal cubic meter of mixed gas at a maximum contraction of 25 percent. Catalyst No. 2 differs from Catalyst No. 1, in so far that it was not dried at room temperature in a vacuum, but instead in the air at 105°C. Thus, the ferrous iron partially 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 No. 1. For this reason, in our future experiments, we will no longer resort to drying in a vacuum.

After mixing the 5Fe-1Cu catalyst with 10 percent basic magnesium carbonate (mixed dry), the yield could be increased to 47 grams (Experiment 3). With an addition of 5 percent aluminum (simultaneous precipitation of the 3 components) 43 grams of liquid products were obtained (Experiment 4). A catalyst consisting of 5Fe-1Cu, containing 20 percent of manganese and for which the components were precipitated simultaneously with sodium bicarbonate, a yield of 48 grams was obtained.

Precipitation from Salts with Soda Without Alkalization Thereafter.

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

Table 2.

Activity of Copper-Containing Iron Catalysts
Prepared from FeSO₄ respectively FeCl₂ by Precipitation with Na₂CO₃

Exp. No.	Catalyst Composition	Preparation Conditions	Exp. Temp., °C.	Maximum Contraction Percent	Days	Max. yields in g./cm of mixed gas
1	5Fe - 1Cu	FeSO₄ and Cu(NO₃)₂ precipitated in the cold with Na₂CO₃	242	14	6	14
2	" "	" "	250	23	5	25
3	5Fe-1Cu-1Mn	FeSO₄,Cu-Mn-nitrate precipitated in the cold with Na₂CO₃.	240	14	4	22
4	" " "	FeCl₂,Cu-Mn-nitrate precipitated in the cold with Na₂CO₃.	240	22	3	32
5	" " "	" "	235	20	4	30
6	" " "	FeCl₂,Cu-Mn-nitrate precipitated in the cold with Na₂CO₃, catalyst extracted for 24 hours with water.	235	12	4	18

Experiments 1 and 2, in Table 2, show that the efficiency of the catalyst produced from iron-sulfate is lower than that of the catalysts produced from ferrous formeate. The yield amounted only to 14 g./m³ of mixed gas at 242°C., and of only 25 g./m³ 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 FeCl₂ was used instead of FeSO₄, 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 catalytic activity of the catalysts produced from FeSO₄ and FeCl₂ could be explained by attributing it to unfavorable influences caused by the presence of some Na₂SO₄ respectively NaCl. For this reason, Catalyst 5 was washed for 24 hours with water before it was used for the operation proper. The washing with water was supposed to remove the last traces of the sodium salts. The wash-water contained definite quantities of chloride irons. Experiment 6 shows that this extracted catalyst does not work any better than the unextracted catalysts; 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 either by washing, as could be seen by comparing it with an unwashed catalyst of the same kind. 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 operation following the precipitation with soda, there are certainly some traces of alkali left in the catalyst which could cause an activation of the contact. By a further washing operation (extraction) with water, the alkali contents are 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, it is possible that the alkali remaining in the catalyst after a normal washing operation may not produce a sufficient activation simply because it is combined with chlorine. This would serve as an explanation for the low activity of catalysts prepared from $FeSO_4$ respectively $FeCl_2$. A better efficiency of the catalyst, however, is not obtained either when the contact precipitated with soda was boiled three times with a soda solution prior to 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 by the experiments described in the following section.

b. 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 3, 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. (Experiment1) to 230°C. Experiments 3 and 4 give the results with catalysts of identical composition which, however, were precipitated from a $FeCl_2$ solution instead of a $FeSO_4$ 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 amounted to 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 which was produced from ferric nitrate as a starting material gives a catalyst of lower activity (for the same conditions of preparation). A catalyst which was obtained by thermal decomposition of the nitrates and which was 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 which 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 which was precipitated out of 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 which were 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. In order 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 to the previous catalyst only yielded 35 grams of liquid products. Experiments 13 and 14 fi-

nally disclose that the addition of magnesium (simultaneous precipitation of the chlorides) reduces the activity of the 5Fe-1Cu catalyst.

Table 3.
Influence of the Addition of Potassium Carbonate

Exp. No.	Catalyst composition	Mode of preparation	K_2CO_3 contents referred to iron	Exp. Temp., °C.	Max. contraction, percent	Max. yields in g./m³ of mixed gas
1	5Fe-1Cu-1Mn	FeSO₄,Cu- and Mn-nitrate precipitated in the cold with Na₂CO₃	without	240	14	22
2	" " "	" " "	1/2%	230	29	43
3	" " "	FeCl₂,Cu- and Mn-nitrate precipitated in the cold with Na₂CO₃	without	240	22	32
4	" " "	" " "	1/2%	230	30	48
5	" " "	FeCl₂,Cu- and Mn-nitrate precipitated with NaHCO₃	1/2%	232	28	45
6	" " "	Fe(NO₃)₃,Cu- and Mn-nitrate precipitated with Na₂CO₃	1/2%	232	25	35
7	" " "	Fe-Cu-Mn-nitrate thermally decomposed	1/2%	232	17	24
8	" " "	FeCl₂,Cu- and Mn-nitrate precipitated hot with Na₂CO₃	1/2%	230	32	51
9	" " "	" " "	without	240	23	40
10	" " "	FeCl₂,CuCl₂ and MnCl₂ precipitated hot with Na₂CO₃	1/2%	233	30	50
11	5Fe - 1Cu	FeCl₂, CuCl₂ precipitated hot with Na₂CO₃	1/2%	235	30	50
12	" "	" " "	without	235	22	35
13	5Fe-1Cu-1/2Mg	FeCl₂,CuCl₂,MgCl₂ precipitated with Na₂CO₃	1/2%	235	23	37
14	5Fe-1Cu-1Mg	" " "	1/2%	235	21	33

(ONE PAGE MISSING)

The optimum K_2CO_3 contents lies somewhere between 1/4 and 1/8 percent. The yields of liquid hydrocarbons amounted to 53 g./m³ of mixed gas, whereas the other catalyst (comparative catalyst) containing 1/2 percent K_2CO_3 only yielded 50 grams. The time of induction for the catalyst to reach maximum activity was one to two days for 1/4 to 1/8 percent K_2CO_3, and three 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 down to 225°C., without changing the catalyst activity noticeably.

Table 4.
Influence of K₂CO₃ Quantity Upon the Activity of the 5Fe-1Cu Catalysts

Exp. No.	K₂CO₃ contents, percent	Exp. Temp., °C.	Max. contraction percent	Max yields in g./m³ of mixed gas	Contraction Percent	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 K₂CO₃ exerts a favorable influence upon the lifetime of the catalyst. The last column of Table 4, shows the contraction which was still obtained after a certain length of operation. The catalysts with 1/16, 1/8, and 1/4 percent K₂CO₃ contents still give a contraction of 28 respectively 26 percent after 40 days of operation, whereas a comparative catalyst with 1/2 percent K₂CO₃ only furnishes 18 percent contraction after 21 days of operation, and 7 percent contraction after 32 days. With the addition of one percent K₂CO₃, the activity decrease is expected to occur even faster, but a contraction of 29 percent was still obtained, after 6 days only 20 percent though, and after 9 days only 6 percent contraction was measured (Experiment 6). The activity of a catalyst containing 2 percent K₂CO₃ was such that within 4 days the contraction decreased from 22 to 7 percent. The lifetime of a catalyst which 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 one-reached maximum contraction of 21 percent remained practically unchanged.

Table 5.-
The Influence of K₂CO₃ Quantity Upon the Lifetime of the Catalyst
(5Fe-1Cu Catalyst)

Exp. No.	K₂CO₃ Contents	Yields, g./cm 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 5 shows very explicitly the favorable influence which small K₂CO₃ quantities (varying from 1/16 to 1/4 percent) have upon the lifetime 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 K₂CO₃, still 47 grams of liquid products per cubic meter of mixed gas were obtained, with a catalyst containing 1/8 percent K₂CO₃, 45 grams, and with another catalyst containing 1/4 percent K₂CO₃, still 37 grams of liquid products per cubic meter of mixed gas were formed. The average yield for six

- 8 -

months is approximately 50 g./m³ of mixed gas for all of these catalysts. It should be taken into consideration that the recorded yields are not referred to standard conditions (0°C., 760 mm.). By referring to normal conditions, the yields seemed higher by about 10 percent. This data was 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 already 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 which 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 remains constant; after 49 days, still 35 grams of liquid products were obtained (see curves 1 and 2).

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

Table 6.

Influence of K_2CO_3 Quantity and Length of Operation Upon the Ratio, $\frac{Yield}{Contraction}$

Exp. No.	K_2CO_3 contents, percent	Days of operation	Contraction percent	Yields in g./m³	Yields/contraction after 7 days	Yields ÷ contraction after days			
						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 5, 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.

In order to find out whether there is a relationship between the yield and contraction, Table 6 shows the ratio of yield to contraction for various catalysts containing varying amounts of K_2CO_3.

After 7 days of operation, the value of the ratio of yield to 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, namely 1.8, refers to the catalyst containing the greatest amount of K_2CO_3. With increasing time of operation, the ratio yield to contraction decreases rather fast 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 the 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.

4. **Effect Which the Mode of Alkalization has Upon the Reaction.**

Up to now the K_2CO_3 addition had been undertaken after the catalyst had been dried. The catalyst was mixed with the K_2CO_3 solution to form a heavy paste, then it was carefully dried on the sand bath. We have also mixed the moist catalyst paste (as is obtained after washing) with the K_2CO_3 solution, and have dried the mass at $105°C$. We found that this mode of addition does not effect the characteristics of the catalyst to any noticeable degree. This may be seen from experiments 1 and 2 in Table 7. 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 7.

Influence of the Mode of Alkali Addition

(5Fe-1Cu-Catalyst)

Exp. No.	K_2CO_3 content, percent	Conditions of preparation	Exp. Temp., °C.	Max. con- traction	Max. yields in g./m³ of mixed gas	Average yield	
						g./m³	Days
1	1/4	Dry cat. 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 impreg- nation with K_2CO_3.	229	30	58	-	-

We also have added one percent K_2CO_3 to a not yet dried catalyst, then we washed the resulting mixture twice with water through a filter funnel. This catalyst behaved just like a catalyst which 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 6 times as was usually done, but was washed 9 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 6 times, we are justified to assume that it is sufficient when the catalyst is washed only 6 times.

5. **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 the large scale, however, the synthesis may only be carried out with a catalyst having a definite form. When the dried catalyst is broken up into little pieces, they do not possess sufficient rigidity to be used success- fully. However, it is possible to produce small pellets by protruding the wet catalyst through small holes. These pellets exhibit excellent mechanical prop- erties. Furthermore, we succeeded in getting a catalyst of good mechanical properties by adding 10 percent of starch[3] (referred to iron metal). The ac-

[3] Brennstoff Chemie, 14, 49, (1933).

tivity of these catalysts may be observed from Table 8. For the sake of comparison, the results obtained with this catalyst are compared with those of a powdered catalyst which had the same composition.

Table 8.

Influence of Shape

(5Fe-1Cu-catalyst)

Exp. No.	K_2CO_3 content, percent	Conditions of preparation	Exp. Temp., °C.	Max. contraction, percent	Max. yields in g./m³ of mixed gas		Average yield in g./m³ in
					7 days	14 days	28 days
1	1/4	Catalyst used as a powder.	229	31	58	58	52
2	1/4	Catalyst containing 10% starch "		31	59	59	53
3	1/4	Catalyst pelleted "		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 the activity of the catalyst containing starch were still approximately equal (average yield 52 respectively 53 grams), 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 it does 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.

6. Influence of the Addition of Na_2CO_3

After we had investigated the effect of K_2CO_3 addition upon the activity and the lifetime 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 are capable of increasing the activity of iron-copper catalysts which were produced by decomposing the nitrates. The increase in activity resulting from the addition of Na_2CO_3 is not quite as pronounced as the increase in activity of K_2CO_3 however[4]

- -

[4] Ges. Abhandlgn. zur Kenntnis der Kohle, Band 10, Seite 389.

- -

The lifetime of the catalysts containing Na_2CO_3 was longer than that of the catalyst containing K_2CO_3.

Table 9.

Influence of Subsequent Addition of Na_2CO_3

Exp. No.	Catalyst composition	Na_2CO_3 content, percent	Yield in g./m^3 of mixed gas in days				
			8	12	19	30	38
1	5Fe - 1Cu	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 9 shows the results with a 5Fe-1Cu catalyst which was 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 were added. With 1/4 percent of Na_2CO_3, the maximum yield of 54 grams was obtained after approximately 12 days of operation (Experiment 1). When this catalyst is compared to one containing 1/4 percent K_2CO_3, it is observed that the percent contraction increases at a much slower rate for a catalyst containing Na_2CO_3. If the yields and the lifetime are just as good as in the case of a K_2CO_3 catalyst, it is to be preferred to use K_2CO_3 as a promotor 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 a Na_2CO_3 content of one percent, the activity decreases and especially the lifetime of the catalyst drops considerably (Experiment 3). This is even more pronounced when 2 percent of 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.

7. Influence of Copper Contents.

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 also copper-deficient iron catalysts. Table 5 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 10.

Influence of K_2CO_3 Upon a 20Fe-1Cu Catalyst (5 percent Cu)

Exp. No.	Catalyst composition	K_2CO_3 content, percent	Yields in g./m^3 of mixed gas after days					
			7	14	21	28	35	42
1	20Fe - 1Cu	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. By referring to Table 4, (Experiment 1) it may be seen that it surpassed the corresponding catalyst containing 20 percent of copper. The catalysts used in Experiments 2 and 3 containing 1/8 respectively 1/4 percent 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 K_2CO_3 (Experiment 4) is of the same order of magnitude as that of the iron catalysts containing 20 percent copper.

It has to be pointed out 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 lesser amounts.

III. Iron-copper 3-component Catalysts Prepared from Ferric Compounds.

At the same time when we investigated the iron-copper catalysts prepared from ferrous salts, we also carried out experiments on 3-component catalysts. The third component consisted of a difficultly reducible oxide, preferably manganese oxide. Earlier, we found that the addition of such an oxide to cobalt and nickel catalysts caused a considerable improvement. This lead 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 pointed out here that the specific action of the manganese oxide is not known up to the very day. It appears that the presence of such an oxide in iron-copper catalysts would not be required so far as improvements in yield and regeneration are concerned, but it seems that the presence of such an oxide has a favorable effect upon the lifetime of the catalyst. Obviously all those factors are also a function of the mode of preparation of the catalyst and the choice of the working conditions.

A. 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 was prepared to contain iron metal, copper metal, and presumably MnO (manganese oxide) in the ratio of 4:1:1.

1. Thermal Decomposition of the Nitrates.

We investigated catalysts which were prepared by decomposing the nitrates at 250-300°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 which were investigated later. The decomposition catalysts were investigated at temperatures ranging between 235 to 250°C. In all cases, it was recognized to be of advantage to add approximately 0.2 to 0.3 or 5 percent of K_2CO_3 to the catalyst. The alkali was added in one case to the nitrates as such and in another case to the finished

catalyst, subsequent to 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 to 1.6. Consequently, it was much higher than that of the later NaOH precipitated catalyst which had corresponding apparent densities varying between 0.92 to 1.17.

For a catalyst quantity corresponding to 4 grams of iron 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 240-250°C. The maximum yield of liquid products ever recorded was 42 g./cm. The lifetime of the catalyst was short on account of the high reaction temperature of 250°C. Already during 20-40 hours, the contraction decreased by 5 percent, and at the same time, the oil and paraffins formed became yellow in color. The lifetime 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 products under normal circumstances, we did not observe a water formation, but only when the average gas velocity came down as low as 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 Section VIII.

The reaction gas of the decomposition catalysts contained a high percentage of CO_2 and H_2 (just as in the case of the precipitated catalysts to be described later). An end-gas which was obtained at 240°C. and 4 liters per hour and a contraction of 25 percent, had the following composition:

	CO_2	sKW	O_2	CO	H_2	CH_4-KW	C-Zahl	N_2
Percent	18.4	1.4	0.3	8.3	59.1	3.7	1.51	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 lower rate than a freshly prepared catalyst. When the alkali-free decomposition products were repeatedly treated with air, it was observed that the activity of these catalysts slowly increased more and more after each regeneration.

   2. Precipitation with Alkalies.

When we resorted to preparing the Fe-Cu-ZnO 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 on we used alkali carbonates.

a. Precipitation with NaOH, (KOH and NH_3).

NaOH. A solution of the nitrates in approximately the 10-fold weight of water (referred to the Fe-Cu-MnO quantities in the nitrates) were precipitated in portions with a hot solution of NaOH under stirring and shaking. The NaOH solution was prepared by dissolving a theoretically required quantity of NaOH + 5 percent excess in four times its weight of water. The filtered precipitate was washed 4 times with the same amount of water as the original liquid amounted to. Although such a catalyst still contains some residual alkali as could be detected by analysis, is 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 still moist but already 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 one 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 lifetime. This apparently is due to the fact that the increased alkali contents favor the formation of high molecular weight hydrocarbons which decompose and cause damaging decomposition products to be left behind on the catalyst. When catalysts were used containing a higher amount of alkali, it could already be recognized superficially that a greater quantity of solid paraffins appeared at the end of the reaction tube and in the receiver.

The following experiment also shows that with the higher alkalized catalyst larger paraffin quantities are retained than in the case of a catalyst carrying the normal alkali contents. A catalyst quantity was used which contained 20 grams of iron, 5 grams of copper, and 5 grams of manganese oxide which in one case contained one percent K_2CO_3, and in another, contained 2.5 percent K_2CO_3. After 360 hours of operation (at 220-230°C. and 2 liters per hour of gas), an 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 which speaks for its greater polymerization ability. 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 one 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 higher alkalized catalyst. A final calculation and addition of all products formed, showed that in both cases approximately the same quantity of synthetic products were formed. For the catalyst containing one percent K_2CO_3, this total quantity amounted to 49.9 grams, and for the catalyst containing 2 percent K_2CO_3, the total yield was 51.5 g./m³ (apparently should be 2.5 percent K_2CO_3).

Compared with the decomposition catalysts, the NaOH precipitated catalysts distinguish themselves in that they may be taken into operation with a fair degree of safety already at 235°C., in some cases even already at 225-230°C., and when large catalyst quantities are used (such as for instance 30 grams), the initial temperature may be as low as 220°C. When a catalyst quantity corresponding to 10 grams of iron, 2.5 grams or copper, and 2.5 grams of MnO (plus 1 percent K_2CO_3) are 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 lifetime 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 inferior to the soda precipitated catalysts in so far as the lifetime is concerned. For example, we found that a NaOH precipitated catalyst working at 220-230°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 irrespective whether a NaOH precipitated catalyst was used or a decomposition catalyst. Primarily, CO_2 was formed and normally little water formation was observed. Detailed data on the relationship between yield, CO_2, and water formation for the NaOH precipitated catalysts are summarized in Section VIII, Tables 19 and 20. When the precipitation of the NaOH catalysts was carried out in the cold with a subsequent washing with hot water, a catalyst was obtained which gave a higher contraction more rapidly, however, the contraction fell off already after 50 to 60 hours of operation. In addition to this decrease of contraction, the reaction products were yellow in spite of the fact that the temperature was only 220°C. This phenomenon is ordinarily observed to occur between 240-250°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 stability of the catalyst is not very good.

A similar observation was made when the constituents of the Fe-Cu-MnO catalyst are precipitated separately with NaOH out of the hot solution. The washed precipitates were then mixed in a moist state by using a mortar and pestle and one 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 of the catalyst described above. We then were in a position to demonstrate that by washing each constituent more intensively than would have been done otherwise, a catalyst of normal character was produced. It appears that with separate precipitation, larger residual quantities of alkali remain in the catalyst than do when the precipitation is carried out simultaneously.

In order to further investigate the influence of the residual alkali contents in the catalyst upon the activity and the lifetime of the catalyst, the following experiment was carried out: A catalyst quantity which contained 40 grams of iron and was prepared by precipitating the various constituents separately was divided into 4 catalytic tubes. Sample No. 1 was used immediately as such without further alkali addition. Sample No. 2 was alkalized with one percent K_2CO_3. Sample No. 3 and Sample No. 4 were first extracted for

24 hours in the soxhlet apparatus in order to extract any possible residual salts originating from the precipitation. As the extraction medium, we used water. After this, Sample No. 3 was immediately taken into operation as it was, but one percent K_2CO_3 was added to Sample No. 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 No. 1 (without alkalization) reached a maximum contraction of 26 percent and remained there for 180 hours. Sample No. 2 (with addition of alkali) reached a maximum of 32 percent contraction very soon, but already after 116 hours yielded yellow reaction products. After 188 hours the contraction had decreased to 20 percent. Sample No. 3 (extracted with water, without alkali addition) gave a contraction of 17 percent and was very active. However it retained this activity all through the duration of the experiment. Sample No. 4 (water extracted with alkali addition) proved to be best. It gave a contraction of 28 percent which is somewhat less than Sample No. 2, but it was essentially more stable, and after 188 hours still caused a contraction of 27 percent. It may be said summarily that the catalyst which was prepared by separate precipitation obviously on account of its comparatively high residual alkali contents was quite active even without the addition of extra alkali. It was rather stable, too. By adding some additional alkali, its activity was increased somewhat more, but its lifetime considerably suppressed. When the catalyst which was prepared by separate precipitation was water-extracted, it decreased considerably in its activity. This is obviously a result of the more efficient was of washing out the residual alkali when each constituent is washed separately. When this water-extracted catalyst was alkalized in the ordinary manner, a comparatively good and stable catalyst resulted. According to this, a good NaOH-precipitated catalyst should be obtained in the following way: 1, by separate precipitation; 2, by a 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 seems to be comparatively active also without additional alkali. The reason for this may be that the residual potassium remaining in the precipitated catalyst acts as a stronger base than the NaOH, and consequently as a greater activating influence. When an additional amount of 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. The process of precipitation with ammonia seems a little more difficult here because the precipitation of the manganese has a tendency to be incomplete, or it may happen that the soluble copper complex salt forms already. One can prevent this difficulty when one precipitates the three constituents separately, and after washing them carefully, mixes them together in a moist state. Without the addition of alkali, the ammonia catalyst was only moderately active, with one percent K_2CO_3 it had acquired the activity of the NaOH catalyst.

b. Precipitation with Na_2CO_3 ((K_2CO_3, $(NH_4)_2CO_3$.)

Na_2CO_3. The preparation of the soda contacts was carried out in a similar manner as the preparation of the NaOH contacts: Fe-Cu, and an Mn-nitrates were dissolved in ten times their weight in water (referred to iron, copper, and manganese oxide contents) and precipitated hot with a hot solution of Na_2CO_3 in water (the solution contained 5 percent excess over the theoretical amount of Na_2CO_3). The soda solution contained one part by weight of anhydrous soda to five parts by weight of water. The precipitate was washed 5 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 pre-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 reduction took place chiefly over CO_2 formation. As an example, in the following table, a soda precipitated Fe-Cu-MnO catalyst containing 0.1 percent K_2CO_3 is described (Fe:Cu: MnO = 10:2.5:2.5).*

Table 11.
Conversion (Mixed Gas) with Fe-Cu-MnO-0.1 percent K_2CO_3 (with Soda Precipitated) 10:2.5:2.5

Temperature, °C.	235	235
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 (diff.)	48.9	50.1
CO_2:Synthesis	1 : 1.2	1 : 1.3
O_2 conversion		
percent going to CO_2	81.2	76.4
percent going to H_2O (diff.)	8.3	11.9
H_2O:CO_2	1 : 9.8	1 : 6.4
Liquid products, g./m³	not determined	52

Table 11 shows that the catalyst after 168 hours of operation still gives the same (somewhat higher) conversion as it did after 46 hours. The yield of liquid products amounted to 53 g./m³. The conversion ratio between CO and H_2 are approximately the same as those of Section VIII, 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. 76 to 81 percent of the CO-oxygen went to CO_2 and only 8 to 12 percent went to water. According to this, a lot of CO_2 and H_2 should be found in the end-gas. This is clearly brought out by the end-gas analysis after 168

*The added K_2CO_3 quantity is referred to the Fe-Cu-MnO quantity.

	CO_2	sKW	O_2	CO	H_2	CH_4KW	C-Zahl	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 10 grams of iron at a gas rate of 4 liters per hour, 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 already sufficient. When a larger quantity of K_2CO_3 is added (up to 2 percent) a soda catalyst is produced which has an initially higher activity which fact can be recognized in the more rapid increase of contraction. However, the lifetime of the catalyst decreases. With higher alkali contents, the formation of the yellow-colored reaction products sets in earlier. The appearance of these yellow-colored substances announces in advance the following decrease of catalyst activity.

The soda-precipitated Fe-Cu-MnO catalyst seems to be more sensitive than the corresponding NaOH catalyst. At a temperature of 245 to 250°C., the catalyst begins to lose its activity comparatively fast.

Experiments extending over a longer period of time and investigating the lifetime and ability to regenerate the soda catalyst were not carried out so far. For the 200 hours for which these experiments were carried out, the soda catalysts proved superior to the NaOH catalysts as far as lifetime is concerned.

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 a 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 one percent) has has a promoter. We observed that the weaker base (Na_2CO_3) remained without influence, also potassium acetate had no influence. However, no damaging effects resulted from their addition. The addition of Rb_2CO_3 caused the appearance of the yellow-colored reaction products to occur earlier. 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. For the precipitation with ammonium carbonate the same may be said as for the precipitation with ammonia. In order to avoid incomplete precipitation or the formation of the water soluble complex salt, it is recommended here to carry out the precipitation of the various components separately, and then mix them together in a moist state.

The behavior of the catalysts precipitated with ammonium carbonate but not impregnated with alkali is described in greater detail in Section VIII in connection with the question whether a relationship exists between the CO_2 formation of the iron catalyst and its alkali contents.

The Fe-Cu-MnO catalysts not treated with alkali add 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 similar to the Na_2CO_3 catalysts, 0.1 to 0.2 percent had to be added. We found that this quantity is also sufficient for the catalysts precipitated with ammonia 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.

3. Variation of the Copper and Manganese Contents in the Fe-Cu-MnO catalysts.

In the previous experiments, results were obtained exclusively with a catalyst containing Fe-Cu- and MnO in the ratios of 4:1:1. We have also carried out some qualitative experiments to investigate how far the copper and manganese contents of the catalyst can be varied without losing any appreciable activity of the catalyst. We have carried out such an experiment in which we used the percent contraction as a measure of catalyst activity, and we have found that the ratio of copper and manganese to the iron may be changed in wide limits without causing essential 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 catalyst quantity was chosen so as to provide always the same quantity of iron (8 grams). (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 contents of the catalyst changed). We worked at an experimental temperature of 250°C. in order to be in a better position to study the stability and lifetime of the catalyst more rapidly. We used the following:

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

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

1	2	3	4
25%	26%	25%	20%

The contraction decreased to 80 percent of the maximum contraction after hours:

420	450	420	440

With the exception of the somewhat weaker catalyst No. 4, all catalysts behaved very similar. On the scale of the present experiment, it made little difference whether the iron contents of the catalyst varied between 33 and 62 percent, the copper contents between 7.7 to 33 percent, or the manganese oxide contents between 29 to 44 percent. It should be mentioned here that catalyst No. 1, still gave 42 grams of liquid products per cubic meter after 447 hours of operation, whereas catalyst No. 3 gave only 37 grams of liquid products per cubic meter.

A further series of experiments brought out that the copper and manganese contents of the catalyst may be reduced down to a very low percentage, and as Section XV reports, these constituents may be missing entirely if one is willing to adjust the experimental conditions accordingly and be satisfied with the longer time which is required for such a catalyst to reach its maximum performance.

In the following, two such copper and manganese oxide-deficient catalysts are mentioned, having composition (1) Fe to Cu to MnO being equal to 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 allowed to work for a short time at 225°C. and gave a 22 percent contraction. When the temperature was raised again to 230°C., the catalyst kept on working for another 298 hours, and continued to give a contraction of 24 percent. The catalyst which was precipitated with ammonium carbonate Fe-Cu-MnO = 10:0.2:0.2, performed essentially slower. 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 only increased very little. But apparently after 12 days of operation, a maximum contraction had not been reached as yet.

Although the experiment described here has no practical significance, it brings out the interesting fact nevertheless, that it is possible to slowly activate 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.

4. Significance of Alkali Addition to the Fe-Cu-MnO Catalyst.

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 or are only mediocre at best. These catalysts require an additional quantity of approximately 0.5 percent alkali, and, we believe that K_2CO_3 so far seems to be the best salt we used. The situation is not quite as clear in the case of the precipitated catalysts precipitated with alkali hydroxides or alkali carbonates. In this case, in spite of the fact that intensive washing is carried out, a certain quantity of residual alkali remains back in the catalyst, which already acts as a promoter and which is already capable of restoring the catalyst activity up to its entire strength. 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 for 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 between considerable limits. If an additional quantity of alkali such as K_2CO_3 is added to such a catalyst still containing considerable residual alkali, the extra addition of alkali might not have any beneficial effect. In some cases, the effect is even damaging, and the impression is created that an alkalization of the catalyst is not required. In order to exclude the varying effects which the residual alkali has, it will be advantageous to wash the precipitate as well as possible with water or it might be possible to extract with water. After extraction, 0.1 to 0.2 K_2CO_3 should be added.

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

The question was raised whether manganous oxide may be replaced in the Fe-Cu catalyst advantageously by other oxides such as tin, chromium, aluminum, or zinc. So far only orientating 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:

$$1. \quad \underset{8:2:2}{Fe-Cu-Cr_2O_3} + 0.5\% \ K_2CO_3.$$

$$2. \quad \underset{8:2:8}{Fe-Cu-Cr_2O_3} + 0.5\% \ K_2CO_3.$$

Catalyst No. 2 was practically inactive and at 240°C., gave only 8 percent contraction. Catalyst No. 1, gave 18 percent contraction at 240°C. and 28 percent at 250°C. After an oxidation with air at 250°C. neither of the catalysts could be used any longer. It did not do any good either to treat with H_2 in order to eventually reduced any forming chromate, although the reduction temperature was 400°C. The corresponding decomposition products, having composition 1 and 2, were even less active than the given precipitated catalysts.

Aluminum. By precipitation with soda from the nitrates, a Fe-Cu-Al$_2$O$_3$ was prepared. This catalyst gave a maximum contraction of 25 percent and lost its activity very rapidly. When the catalyst was impregnated with one percent K_2CO_3, the contraction only came up to 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 meta-stannic acid (from tin, nitric acid). The catalyst was almost entirely

inactive, in both cases only a very slight formation of oil resulted. No noticeable contraction was noticed at 250°C. The catalyst had the following composition: Fe-SnO-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.

C. Appendix.

In addition to the Fe-3-component catalysts, we desire to describe a few more experiments in which catalysts of a special composition or a certain preparation were investigated.

Iron Manganese. The following experiments show that iron-manganese catalysts which do not contain copper exhibit a certain activity when used at 235°C. A catalyst which was precipitated with soda and consisted of Fe and MnO in the ratio of 10:2.5 and contained 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 (gas charge, 4 liters per hour of mixed gas). After 69 hours, the reaction products became yellowish in color and after 114 hours, the contraction started to decrease again.

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 after 162 hours, 18 percent was observed. After 210 hours, the contraction was 20 percent, the maximum contraction at 235°C. When the temperature was raised to 240°C., the contraction could be increased to 25 percent (after approximately 282 hours altogether). A previous reduction with H_2 at 350 to 400°C. (1-1/2 to 2 hours of treatment), was of no influence on the alkali-free as well as the alkalized catalyst. Further details on the copper-free iron catalyst are discussed in Section XV.

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

Iron Salts. By precipitating ferric nitrate, respectively ferrous chloride, with disodium phosphate, the voluminous iron-phosphate was obtained. At temperatures up to 260°C. and using mixed gas, the phosphate did not give any contraction. An oxidation at 250°C. and an H_2 reduction at 300-350°C. remained without influence. A so-called 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. When the catalyst was subject to reaction temperatures, considerable quantities of boric acid sublimed away from it. Another borate which we produced by treating ferric nitrate solutions with borax was not effective either. The not-washed preparation yielded for a long time, nitric acid, nitrous oxides, and water, when heated in a stream of mixed gas. Boric acid kept on subliming off.

<u>Iron (2)-carbonate.</u> For the preparation of ferrous carbonate, we mixed lead nitrate with the calculated quantity of ferrous sulfate together 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. The digestion was carried out long enough to convert all the ferrous sulfate. The solution containing a precipitate of lead sulfate was filtered, and the light green clear filtrate containing the ferro nitrate was heated up 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 carried out in a nitrogen atmosphere as well. Nevertheless, a superficial discoloration (oxidation) of the carbonate did set in. When the carbonate was allowed to act on mixed gas, a noticeable contraction could only be observed above 240°C. The maximum contraction of 19 percent was observed at 250°C. Already after 8 hours of operation and after a decrease of activity of the catalyst, the products assumed a yellow discoloration.

(Meyer) IV. Needle-Iron-Ore Catalysts.

According to Fricke and Ackermann[5], during the dehydration of synthetic needle

---

[5] Zeitsch r. Electrochemie 40, 630, (1934).

---

iron ore ($\alpha Fe_2O_3 \cdot 1H_2O$) one obtains α iron III oxides of greater internal energy contents, the lower one keeps the dehydration temperature. 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 randomness of the 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 the Synthetic Needle Iron Ore ($\alpha Fe_2O_3 \cdot 1H_2O$)

In the preparation of the needle-iron-ore, we resorted to the method of Fricke and Ackermann.

A solution containing one mole of iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) in one 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 oxy-hydrate was washed 7 times, each time with 4 liters of water. The separation of wash-water from precipitate was accomplished by decantation and consequent pressing. All operations were carried out in the cold. Before being dried, the moist and amorphous mass of oxyhydrate was mixed with twice its quantity of concentrated KOH solution. Then the mixture was heated for 2 hours to 140-160°C. in a silver-lined autoclave. The reaction product which was bright yellow in color was filtered off and washed with water 6 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 having been washed carefully 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 one liter per hour, the needle-iron-ore catalyst gave a contraction of 29 percent and a yield of liquid hydrocarbons of 25 g./m³ 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 phosphorous pentoxide had apparently no effect upon the activity.

It is pointed out later that 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 lifetime 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) causes the activity to decrease. In the same way, the activity decreases when 1/2 percent K_2CO_3 is added after the copper addition. Since the lifetime 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, it appeared purposeful to increase the catalyst quantity from 4 grams to 10 grams of iron. This measure required no reduction of the gas velocity since the dumped weight of the needle-iron-ore catalyst as compared to cobalt and nickel catalysts is approximately 4 times as great as that of the latter. The following experiments, therefore, refer always to 10 grams of iron, a contact layer length of 30 cm., and a flow velocity of 4 liters per hour.

Table 12 gives the results with a copper-free needle-iron-ore which was dehydrated under various conditions.

As already mentioned with regard to activity, it does 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 contact was taken into operation with mixed gas immediately (Experiments 1 and 2). Previous to Experiment 3, the needle-iron-ore was dehy-

drated 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. It has to be mentioned, however, that the results of this experiment were difficult to reproduce. As the dehydration is carried out in the presence of hydrogen instead of air again at 400°C., the needle-iron-ore acquires only a very slight activity (Experiment 4).

For Experiments 5 to 8, a needle-iron-ore was used which contained 25 percent of copper as carbonate. The mode of mixing the copper into the moist catalyst is described earlier. A maximum yield of 50 grams of liquid products (Experiments 5 and 6) was obtained irrespective whether the catalyst was taken into operation already with mixed gas or whether it was first dehydrated in a stream of air at 210°C. In comparison 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). A dehydration in a stream of H_2 at 400°C. lead to a somewhat smaller activity (Experiment 8). Finally, we investigated the activity of a catalyst where the copper had been added after dehydration of the needle-iron-ore in a stream of air at 400°C. had taken place. The copper was mixed into the catalyst in the dry state. When the results of this catalyst were compared to a catalyst where the copper was mixed into the moist needle-iron-ore, it was observed that the catalyst having been mixed dry showed an activity which was 50 percent below the activity of the moist catalyst (Experiment 9).

We further investigated the activity of a copper-containing needle-iron-ore catalyst containing the corresponding quantity of Fe-Cu in the same ratio as the previous needle-iron-ore copper catalysts but which would contain the $\alpha Fe_2O_3 \cdot 1H_2$) component as 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 into two halves. The first half was converted into needle-iron-ore by applying heat under pressure at a temperature of 150°C. in 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 later on mixed with copper carbonate. Both catalysts were taken into operation with mixed gas without having previously been pretreated. They furnished the results indicated in Table 13. Indeed, the needle-iron-ore catalyst containing the crystallized iron oxide is far superior as far as activity is concerned when compared to the catalyst containing amorphous iron oxide. It was found that the yields for the crystalline catalyst were approximately 3 to 4 times as high as those of the amorphous catalyst. This increased activity may be easily explained by a change of the crystalling structure which takes place within the needle-iron-ore after dehydration. During this dehydration, the water held back by the crystalline structure of the catalyst is either totally or at least partially removed, and by doing so, a random crystalline structure is produced.

With reference to the lifetime of the catalyst, one observes from Table 13, Experiment 2, that the maximum yield was still 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 through the addition of copper to the needle-iron-ore may not be improved any further by the addition of thorium for instance, or Mn. In Table 14, 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 thorium which was precipitated from thorium nitrate with potassium carbonate. The copper-containing needle-iron-ore catalysts prior to the thorium addition had been dried at 100°C. Catalyst No. 2 was prepared in such a manner that precipitated copper and precipitated thorium were mixed together with the needle-iron-ore in a moist state. For Experiment 3, copper-containing needle-iron-ore which had not been dried yet was mixed as a moist paste with freshly prepared thorium. The addition of manganese, Experiments 4 to 6, was carried out in an analogous manner. All catalysts furnished a maximum yield of 49 to 52 p. m³ of mixed gas. A specific influence of the thorium respectively manganese upon the activity of the catalyst could therefore not be observed. Regarding the lifetime of the catalyst, it may be said that the thorium-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 have also investigated the possibilities of preparing it in a simpler manner. We want to report on these experiments shortly. To start with, we endeavored to prepare the needle-iron-ore in presence of precipitated copper in order to produce a more homogeneous iron copper mixture. The preparation of needle-iron-ore in the presence of copper did not succeed. In every instance, we obtained amorphous Fe_2O_3 mixed with CuO, which fact could already 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 and 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 precipitated simultaneously with potassium carbonate respectively sodium hydroxide and when heat and pressure was applied in the presence of potassium hydroxide no needle-iron-ore was produced. The catalytic effect of these products was slight. The highest contraction was 15 percent at 250°C.

Further experiments dealt with a simplified method of producing needle-iron-ore in the absence of copper. Thus, the recommendation by Fricke and Ackermann calling for an intensive washing operation of the amorphous oxyhydrate precipitated with ammonia seems superfluous. It was sufficient to apply one single washing operation with water, and a following application of heat under pressure with KOH thus lead to the needle-iron-ore (one mole of iron was washed with one liter of water). Application of heat under pressure and treatment with NaOH instead of KOH does 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 worked with an autoclave which was of iron or which was lined with copper, no needle-iron-ore was obtained. It is therefore probable that the silver favors the formation of the needle-iron-ore catalytically.

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

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

The investigation of the catalytic behavior of needle-iron-ore catalysts as used for the benzene synthesis may be summarized in 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 g./ml. 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 Section II that the ordinary iron catalysts prepared in much simpler ways have higher activities and especially exhibit longer lifetimes.

Table 12.

Dehydrogenation of Needle-Iron-Ore With or Without Copper Under Various Conditions

Exp. No.	Catalyst 10 g. of iron	Pretreatment	Exp. temp., °C.	Max. contraction percent	Yield g./m^3 of mixed gas
1	Needle-iron-ore	Mixed gas immediately	233	13	12
2	" " "	2 hrs. air, 210°, then mixed gas	"	13	13
3	" " "	16 hrs. air, 210°; 1 hr. air, 400°	"	28	41
4	" " "	16 hrs. H$_2$, 210°, 1 hr. H$_2$, 400°	"	2	almost inactive.
5	Needle-iron-ore plus 25% copper	Mixed gas at once.	230	31	49-50
6	" " "	2 hrs. air, 210° then mixed gas	233	29	50
7	" " "	16 hrs. air, 210°, one hr. air, 400°	"	28	47
8	" " "	16 hrs. H$_2$, 210°, 1 hr. H$_2$, 400°	"	26	40
9	CuCO$_3$ added after treatment with air at 400°C.	16 hrs. air, 210°, 1 hr. Air, 400°.	242	21	26

Table 13.

Influence of KOH Pressure Heat Application As Well As Catalyst Quantity Upon Yield and Lifetime

No.	Catalyst 10 grams of iron	Exp. Temp., °C.	Max. con- traction percent	Max. yield g./m³ of mixed gas	Yield in grams after		
					12 days	22 days	42 days
1	Fe precipitate. with ammonia after KOH treatment at room temperature with CuCO₃. 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 CuCO₃.	230	30	49	47	41	--
3	Catalyst identical with No. 2, but with 20 grams of iron.	230	31	51	49	48	37

Table 14.

Influence of Various Additions to the Copper-Containing Needle-Iron-Ore

No.	Added to the needle-iron-ore	Mode of addition	Exp. Temp., °C.	Max. con- traction, percent	Grams of liquid products/m³ of mixed gas	Remarks
1	25% Cu, 18% ThO₂	Needle-iron-ore plus Cu (at 100°C. dried) mixed with freshly precipitated thorium.	230	31	52	After 17 days, still 48 grams obtained.
2	"	Cu plus thorium precipitated simultaneously with K₂CO₃ washed and mixed in moist state with needle-iron-ore.	234	29	51	After 18 days, still 41 grams obtained.
3	"	Precipitated Cu mixed moist with needle-iron-ore; to this, moist precipitated thorium is added.	235	30	49	After 17 days, still 43 grams obtained.
4	25% Cu, 20% Mn	Needle-iron-ore + Cu (at 100°C. dried) mixed with freshly precipitated manganese in moist state.	234	29	50	--
5	"	Cu and manganese precipitated simultaneously and mixed with needle-iron-ore in moist condition.	232	29	51	After 18 days, still 35 grams 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, still 33 grams obtained.

(Meyer)   a. Influence of CO pretreatment.

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. The maximum activity is reached after a certain time of induction elapses which for the alkalized catalysts with increasing alkali contents becomes shorter. As already mentioned, the time of induction for a catalyst containing 1/4 to 1/8 percent K_2CO_3 is a maximum of one to 2 days. At 1/16 percent K_2CO_3 approximately 3 days are required. For the catalysts which do not contain excess alkali, the time of induction may be as high as 14 days.

We have investigated the question whether by a special pretreatment of the catalyst a better activity could be obtained or whether the time of induction could be shortened. Experiments 1 to 4 of Table 15 were carried out with Fe-Cu-Mn catalysts which were prepared by precipitating $FeCl_2$, $CuCl_2$, and $MnCl_2$ with soda. An additional 1/2 percent K_2CO_3 was used for impregnation.

Catalyst No. 1 was taken into operation with mixed gas at once. Catalyst No. 2 was first treated with Co for 24 hours, Catalyst No. 3 was treated with CO for 24 hours. Catalyst No. 4 was treated first with mixed gas for 24 hours and following with H_2 for another 24 hours. The pretreatment temperature in all cases was 235°C. The contractions obtained after 25 hours of operation were 5, 17, 28, respectively 31 percent. In the case of Experiment 4, it has to be taken into consideration 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 in so far as the yield of liquid hydrocarbons was concerned, and also in so far as the percent contraction was observed. With respect to the stability of the catalysts, no worthwhile differences could be observed, for in all cases the average yield was approximately the same after 17 days of operation (last column, Table 15). The lifetime of these catalysts was not too satisfactory probably because they contained 1/2 percent K_2CO_3.

(Table 15 - next page)

If a previous pretreatment with CO exerts a favorable influence upon the time of induction of the catalyst (as referred to the moment when mixed gas was admitted) one naturally cannot speak of a reduction of the induction time for these experiments 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 only pretreated for 2 hours. When the pretreatment was carried out with mixed gas and following H_2, the contraction after the same length of time of operation was only 8 percent. The two catalysts, however, do not differ in their maximum activities exhibited. 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 increase in activity of lifetime resulted.

Table 15
Influence of Protreatment with CO

Exp. No.	Catalyst composition	Pretreatment of the catalyst	Exp. Temp. °C.	Percent Contraction after 5 hrs.	Max. contraction, percent	Max. yield, in g./m³ mixed gas	Average yield after 17 days of operation, g./m³ of mixed gas
1	5Fe-1Cu-1Mn +1/2% K₂CO₃	Mixed gas immediately	228	5	30	49	47
2	" "	24 hrs. CO then mixed gas.	228	17	32	50	47
3	" "	24 hrs. CO, 24 hrs. H₂ then mixed gas.	228	18	30	49	45
4	" "	24 hrs. mixed gas, 24 hrs. H₂ then mixed gas.	228	31	30	49	44
5	5Fe-1Cu + 1/2% K₂CO₃	Mixed gas at once.	230	after 2 hrs. 4%	31	55	-
6	" "	2 hrs. mixed gas, 2 hrs. H₂, then mixed gas.	230	after 2 hrs. 8%	32	52	-
7	" "	2 hrs. CO, 2 hrs. H₂, then mixed gas.	230	after 2 hrs. 16%	31	53	-

(Bahr) In addition to the previously described experiments, some further investigations are mentioned in which we investigated how a short pretreatment with CO influences the time of induction of the catalyst, 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 metals in the ratio 10:2.5:2.5. 0.5 Percent of K₂CO₃ had been 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 switched to CO, and the catalyst was allowed to act upon CO for the desired length of time at a flow velocity of 4 liters of CO per hour. Then we lowered the temperature down to the reaction temperature of the experiment which was 230°C. After this, we switched over to mixed gas.

It should be mentioned here that in the experiments carried out, uniform and reproducible results could not always be obtained. Nevertheless, the following findings were made.

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 one to 2 hours, a very great reduction in induction time resulted.

When the pretreatment was carried out for one to 2 hours and 250°C., the catalyst gave 19 percent contraction, after one 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 for the following synthesis at 230°C. already after 1/4 hour, and 22 percent after 3/4 hours, but after 4 hours, the contraction did not go beyond 25 percent.

When the temperature of the CO pretreatment operation was increased some more, as for instance, to 270°C., no further favorable results were obtained. When mixed gas was admitted to such a catalyst, the contractions measured 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 hours, 14 percent, and 18 percent after 2 hours. In some cases, we succeeded to produce a catalyst which reached its maximum contraction comparatively fast 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 hours, 15 percent after 1/2 hr., and 20 percent contraction after 2 hours.

During the CO treatment at 250°C. to 270°C., the following observations were made: Immediately after the passage of the CO, the exit gas showed very high percentages of CO_2 (up to 90 percent). After 1/2 to 3/4 hours, this CO_2 content had reduced drastically, and depending on the temperature, approached a more or less constant value of 10 to 20 percent. Generally, a contraction was not observed in the beginning. At 250°C., and even after one to 2 hours, no contraction was observed. At 260 to 270°C., a contraction gradually set in which could go up as high as 13 percent. Here apparently, a partial decomposition of the CO occurs 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 formation at 235°C. set in generally after 2 to 3 hours. Here, however, the visible oil formation was observed very soon after mixed gas was admitted, and in no case later than after one hour. In most cases we could observe the formation of oil already after 1/4 to 1/2 hours. In some cases, even already 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 remained even below 30 percent, that is, it almost did not increase any further. We also noticed that the pretreated catalysts had a shorter lifetime than the normal catalyst, and that they had a tendency to form yellowish colored 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 one hour and 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 effects upon the contraction.

(Bahr) Pretreatment with Mixed Gas at Higher Temperatures.

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 the following reaction temperature. The investigated temperature range was 250 to 300°C., the time of pretreatment lasted from one to 2 hours. As an example, the following experiments are described.

A Fe-Cu-Mn 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 hours. Then it was heated for another hour at 250°C. with mixed gas. After this time, it furnished 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 hours, 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 the indicated experiments, it is noticeable that pretreatment with mixed gas at elevated temperatures is without advantage. It appears that the 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 unfavorable than the normal 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 already at temperatures of around 250°C.

Influence of H_2 Pretreatment.

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

(Bahr) <u>Hydrogen Treatment at the Reaction Temperature, 235 - 300°C.</u>

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 takes place as well as the reduction of the higher manganese oxides. The reduction of these metals, however, does not proceed down to the metallic state, but only to a lower oxide. In the case of manganese, it leads to MnO.

(Meyer) Influence of H_2 Reduction at High Temperatures.

A preceding reduction of the Fe catalyst with H_2 at high temperatures causes 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., and following action upon mixed gas, a contraction of 14 percent was obtained after one hour. After 24 hours of further operation, the contraction had decreased to 6.5 percent, and yellow-colored products were formed already. Since this catalyst had been reduced by the H_2 treatment at 450°C. already rather far to iorn metal, the deterioration of activity may be due to various reasons. First, the iron which was formed due to the reduction at 450°C. might have sintered. Secondly, the high reduction temperature might have favored the iron and copper to form an alloy one with another.

However, there is an indication that in come 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 entirely active when taken into operation with mixed gas immediately. After a reduction with H_2 at 450°C., this catalyst yielded 27 percent contraction after 8 hours already; however, it had reduced 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 out of the question.

(Meyer) VI. <u>Influence of the Addition of Carriers and Influence of the Mode of Addition.</u>

The addition of carriers is very important when we speak of cobalt and nickel catalysts. It exerts a marked influence upon the activity and lifetime of those 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, an activation is actually caused by the addition of the car-

riers. 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 proceeds in a different course when a carrier is added. Just as it is possible to direct the reaction of water formation, the possibility should exist to increase the yields which are obtained from mixed gas and iron catalyst. In the next chapter, we shall report on these experiments.

a. Fe-Cu-carrier Contacts from Ferrous Salts.

The basic material which was 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 60g./m³ of mixed gas. Table 16 summarizes the results of the 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 of special interest. For Experiment 2, the catalyst which was used in Experiment 1 and 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. In considering for the moment the small maximum yield (51 grams), 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 already decreased to 13 percent after 4 days of operation. A preceding reduction of 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 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 non-alkalized 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 g./m³ 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 respectively 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. With this mode of addition of glass powder, the increase in activity is not as pronounced as we found it to be 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 48 grams.

Table 16

Influence of the Addition of Carrier and Mode of Addition
Precipitation of Chloride with Na_2CO_3; 5Fe + 1Cu Catalyst

Exp. No.	K_2CO_3 contents	Carrier, 4 g. per 10 g. of Fe	Mode of Addition	Reduction Conditions	Max. contraction, percent	Behavior of the catalyst
1	1/4%	without	-	immediately, mixed gas	13 230°	58g., liquid products
2	1/4%	kieselguhr	mixed dry afterwards	"	32 232°	51g., liquid products, induction time, 4 days; faster decrease of activity than in case without carrier.
3	1/4%	kieselguhr	added before precipitation	"	16 240°	Rapid decrease of activity; slight water formation.
4	1/4%	kieselguhr	"	H_2 350°	17 240°	Initially small water formation; only 10 percent contraction after 10 days.
5	without	kieselguhr	"	immediately, mixed gas	16 240°	Initially small water formation; rapid decrease of activity.
6	without	diatomaceous earth powder	added after precipitation	"	16 236°	No H_2O formation.
7	1/4%	"	"	"	22 236°	" " "
8	without	sodium glass powder	added afterwards in dry state	"	29 237°	49g. of liquid products. Na-glass powder does not activate as well as K_2CO_3. Long time of induction.
9	without	"	added after precipitation	"	26 237°	40g. of liquid products. Very slow increase of activity. Mode of addition more unfavorable than dry state.
10	without	"	added before precipitation	"	26 237°	" "
11	without	without	- -	"	22 237°	28g. of liquid products.
12	without	powdered silica gel	added after precipitation	"	15) 240°)	Slight activity
13	1/4%	"	"	"	13) 240°)	Slight water formation. No improvement when reduced with H_2 at 450°C.

Table 16 (cont'd.)

Exp. No.	K_2CO_3 contents	Carrier, 4 g. per 10 g. of Fe	Mode of addition	Reduction conditions	Max. contraction, percent	Behavior of the catalyst
14	1/4g	silica gel powder	added dry afterwards mixed gas	immediately	30 230°	56g. of liquid products. For When silica gel is afterwards mixed in dry, the latter remains indifferent.
15	without	asbestos meal 10g./10g. of iron	after precipitation	mixed gas immediately. H_2 450°	10% 250° 21% 238°	Deterioration due to asbestos powder. Rapid decrease of activity.
16	1/4g	"	"	"	14% 250° 25% 238°	" "

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

Table 17 contains a few more experiments, during which some metal oxides had been used as carriers. Although these metal oxides cannot be considered as carriers proper, 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 decrease the activity of the alkalized as well as the non-alkalized iron-copper catalysts in 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 exerts an unfavorable influence upon the activity of the iron-copper catalyst (Experiments 5 and 6); no difference seems to exist in the activity of the alkalized and non-alkalized catalyst. Finally, we investigated the influence of chromium oxide. Cr_2O_3 behaves indifferent irrespective whether it is mixed with a catalyst in moist or in dry form. The yields with the alkalized and non-alkalized catalysts are of the same order of magnitude as with the catalysts without Cr_2O_3 addition.

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.

Table 17.

Precipitation of the Chloride with Na$_2$CO$_3$

(5Fe-1Cu Catalyst)

Exp. No.	K$_2$CO$_3$ contents	Carrier, 1 g. per 10 g. of Fe	Method of addition	Reduction condition	Max. contraction, percent	Behavior of the catalysts
1	without	MgO	added after precipitation	immediately mixed gas	12 235°	No water; slow increase of activity; MgO acts damaging.
2	1/4%	MgO	"	"	20 235°	" "
3	without	ZnO	"	"	14 235°	No water formation; ZnO acts damaging.
4	1/4%	ZnO	"	"	22 235°	" "
5	without	Commercial Al$_2$O$_3$	"	"	13) 235°)	Deterioration by Al$_2$O$_3$ no water formation.
6	1/4%	"	"	"	13) 235°)	" "
7	without	Commercial Cr$_2$O$_3$	"	"	22 230°	28 g. of liquid products
8	1/4%	"	"	"	29 230°	51g. liq. prod.) Cr$_2$O$_3$
9	without	"	added dry	"	15 230°	27g. " ") behaves almost indif-
10	1/4%	"	"	"	30 230°	54g. " ") ferent

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

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

1. Carrier-Decomposition Catalysts.

In previous experiments we have mixed the carrier material directly to the oxide powder obtained by decomposition of the nitrates. We added about 0.5 percent K$_2$CO$_3$, 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 on, we carried on investigations during which the carrier material was mixed with the nitrates prior to 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 prior to the decomposition. The chief carriers used were Suttgart 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 were approximately as active as the catalyst without carrier. It is interesting to notice that the addition of kieselguhr caused an extraordinary deterioration of the catalyst and it rendered the catalyst almost inactive.

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.

2. Precipitated Catalysts.

By mixing an alkali-precipitated catalyst in a dry state together with a carrier, such as silica gel and kieselguhr, catalysts were obtained which gave approximately the same percent contraction as the carrier-free precipitated catalysts. (We found this information from earlier experiments.) The advantage which we derived through these precipitated catalysts was chiefly that the larger volume of catalyst contained a smaller quantity of metal. It should be mentioned, however, that the lifetime 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 top of the carrier. As long as sodium hydroxide was used, as precipitant, we were not successful in obtaining effective catalysts. For instance, a catalyst which was precipitated on kieselguhr by using NaOH proved to be practically inactive even at 250°C. Also with Na_2CO_3 and K_2CO_3 and the use of kieselguhr, at first, very little active catalysts were obtained. Better results were found with asbestos, calcium carbonate, aluminum silicate, and powdered silica gel. These materials were used 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 on we succeeded in essentially improving the kieselguhr precipitated iron catalysts without recognizing the reasons for the initial failure of this combination.

As is mentioned in Section VIII, 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 contents have been subject to a thorough investigation (no yet concluded).

Fe-Cu-MnO-Kieselguhr Catalysts: Preparation of the Catalyst:

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 is heated to the boiling point, and then the required quantity of kieselguhr is added. A hot solution of Na_2CO_3 is added to the hot nitrate-kieselguhr-slurry under frequent stirring. (The Na_2CO_3 solution contains the theoretical quantity of Na_2CO_3 + 5 percent excess in the tenfold weight of water.) The Na_2CO_3 solution was added to the nitrate-kieselguhr-slurry in portions. After the precipitation is completed, the precipitate is filtered and washed 6 times with hot water. Each washing is equal to the original volume of the original slurry. After the washing operation, the filtrate should react only faintly alkaline. No alkalization of the catalyst was carried out. After the catalyst was predried on the water bath, it was further dried in the oven at 105°C. We have found it purposeful not to take the catalyst into operation with mixed gas at once, but rather to heat it up to the 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.

On account of the larger volume of the kieselguhr catalysts, we were not in a position to use 10 grams of iron as we did in the case of the carrier-free catalyst earlier with normal experiments. We only used 4 grams of iron. Visible oil formation set in 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 hrs., it was 30 percent (maximum contraction). The contact yielded water from the very beginning. Section VIII describes the difference between the kieselguhr catalyst and the carrier-free catalyst for the same contraction. It is mentioned here only that the kieselguhr catalyst only converts 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 our for the 1:1 kieselguhr catalyst, since we found that the lifetime of this catalyst was very short. Already after 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 may not be reproduced very readily. Some catalysts (of same composition apparently) only yielded a contraction of 15 to 20 percent at 235°C. The causes for this unreproducible behavior could not be discovered so far. We suspect that the alkali contents of the catalysts has something to do with that. 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 seems to be extremely variable. Apparently in some instances, the alkali content is higher, in others lower.

We have endeavored to activate such an inactive 1:1 catalyst, for example, by boiling it with water in order to remove the possible unfavorable excess of alkali. No improvement of the catalyst resulted through this measure. It has to be mentioned here, however, that we did not succeed in removing any residual precipitating salts out of 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 stronger alkaline when tested with litmus. After the drying, the catalyst was boiled for some time with water in order to remove the residual alkali. Neither the acqueous filtrate nor the catalyst reacted alkaline when tested with litmus after the boiling operation had been carried out. This was an indication that the residual alkali was held firmly by the catalyst (the kieselguhr) after the drying operation.

Considering that such an ineffective 1:1 kieselguhr catalyst could contain too little alkali, we have taken already dried catalysts and added some additional alkali to them. 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 effected 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.

A 1(4Fe-1Cu-1Mn0):0.5 kieselguhr catalyst was only little active. It only 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 yet pronounced with the small quantity of kieselguhr used.

Better yields than with a 1:1 kieselguhr catalyst were obtained with a 1(4Fe-1Cu-1Mn0):2 kieselguhr catalyst. With the application of only 4 grams of iron in the catalyst quantity 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(inclusive water vapor). Although this yield is smaller than that obtained with the carrier-free precipitated catalysts, the result may be looked upon as favorable anyhow, because it was obtained with the application of only 4/10 of the otherwise customary quantity of iron, and also at a considerably smaller CO consumption. In the present case, approximately 55 percent altogether of the furnished CO were used up. At a complete CO usage, a yield of 85 grams per cubic meter would result. In comparison with this, a carrier-free catalyst gave a yield of 55 grams per cubic meter. 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 contraction of 20 percent was still obtained for 4 liters per hour of gas, and 26 percent contraction for 2 liters per hour. The corresponding yields were 27 respectively 36 grams per cubic meter.

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

Temp., °C.	gas rate liters/hour	Contraction, percent	Liquid products g./m³
215	4.3	28	35
225	4.1	33	55

These results may be looked upon as favorable from the point of view of CO usage, and the water formed during the reaction.

In most cases, the 1:2 kieselguhr catalyst was reproducible. The lifetime of the catalyst so far cannot be regarded as satisfactory up to now. With a catalyst quantity corresponding to 4 grams of iron at an hourly gas rate of 4 liters after already 120 hours at 235°C., a decrease in the contraction was observed. Apparently, a reaction temperature of 235°C. is too high a temperature to employ when working with kieselguhr catalysts. More favorable results were obtained at 225°C., working temperature, although a smaller conversion was observed when the same quantity of iron, namely 4 grams, was used.

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

1(4Fe-1Cu-1MnO):3 kieselguhr catalyst.

When we used this catalyst, we could only charge the tube with a catalyst 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, under the most favorable conditions, a contraction of 28 percent and correspondingly a yield of 45 grams of liquid products per cubic meter. Along with the liquid products, 40 grams of water per cubic meter were formed, so that water and oil were produced in the ratio of 1:1.1. We investigated this catalyst at 235°C., and found more unfavorable results, namely only 30 grams of liquid products per cubic meter, were obtained. This was attributed to the shorter lifetime of the catalyst. The contraction decreased from 30 to 26 percent within 70 hours of operation.

1(4Fe-1Cu-1MnO):4 kieselguhr catalysts.

A further dilution of the catalyst to 1:4 proved to be unfavorable. By doing this, the time of induction of the catalyst was considerably prolonged. For example, such a catalyst when using an equivalent quantity of iron, of 2 grams, and 4 liters per hour of gas, and 235°C., gave 3 percent contraction after 46 hours, 9 percent after 118 hours, and after 142 hours, only 12 percent. At 245°C., such a catalyst containing 4 parts of kieselguhr, 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 as did the previously described catalysts, namely 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 one respectively 0.5 gram of iron 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 the Kieselguhr Precipitated Catalysts.

As has been mentioned in previous paragraphs, the kieselguhr catalysts offer the possibility (even if only theoretical) to increase the yields of liquid products. This is due to the fact that they convert less CO to CO_2 than do the carrier-free catalysts. In order to use the experiences made with the kieselguhr catalysts on the technical scale, 2 hindering properties of the catalysts have to be overcome, namely, the unsatisfactory activity and the comparatively short lifetime.

We have tried by several means to increase 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, or 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 water formation. 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 around 30 percent. When the alkali (K_2CO_3) was added in larger quantities (one percent) to the already dried catalyst (at 105°C.) in some cases, we observed that the alkali addition had even a damaging effect, and it lead to catalysts of lesser activity. Smaller additions remained without influence. If the alkali was added to the still moist catalyst immediately after precipitation, additions amounting to 0.1 to 0.2 percent did not cause any noticeable effect. With additions amounting to 0.5 to one percent, we observed that the reaction showed a tendency to take the course over the CO_2 formation again.

These facts were especially outstanding with catalysts which were precipitated with ammonia. The simultaneous 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 to this catalyst, we could observe that the water formation decreased as the alkali added to the catalyst was increased. With approximately 0.5 to one percent K_2CO_3, the visible water formation stopped entirely.

We have furthermore tried to utilize the mixed gas to a greater extent when using iron-kieselguhr catalysts (in one stage), by using correspondingly wide and longer catalyst tubes and larger catalyst quantities. 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 which was reached in this manner amounted to 37 percent. A more thorough investigation showed why a further increase in contraction is no longer possible. We found that the CO under the given conditions is converted to a large degree

however, not under increased water formation, but rather increased CO_2 formation. It is, therefore, apparent that the carrier catalyst approaches more and more the behavior of the carrier-free metal catalyst when the conversion of the CO increases. In Section VIII, page 114 of the original manuscript, the conversion conditions for a kieselguhr catalyst are 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 are of the opinion that by continuing the experiments with the iron catalysts containing kieselguhr, we may eventually obtain yields which are higher on the average than 55 grams of liquid products per cubic meter.

(Bahr)   VII. Course of the Reaction with the Iron Catalyst.

Between the carrier-free iron catalysts and the cobalt catalysts used for the benzene 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) practically only water is formed. The course of the reaction with cobalt catalysts follows the following equation:

$$CO + 2H_2 = (CH_2) + H_2O$$
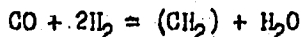
whereas for iron, the reaction chiefly proceeds according to:

$$2CO + H_2 = (CH_2) + CO_2$$
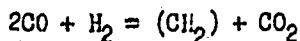
This equation states that with iron catalysts for every molecule of hydrocarbons one molecule of CO_2 is produced, that is, in presence of iron catalysts only 1/2 of the CO goes to synthetic products of some nature. As already pointed out, the reaction with iron catalysts does not proceed exclusively according to the equation given above, but here also, varying with experimental conditions, water is formed to a greater or lesser extent. In general, one can say 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 is for a given catalyst layer length.

In order to bring out the differences between iron and cobalt catalysts more closely, Table 18 shows experiments with an Fe-Cu-MnO catalyst as well as with a cobalt-manganese and 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 the analysis of the reaction gases under consideration of the contraction. In this way, the percentage of the converted CO is found also. 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 and originating from the CO. In order to ascertain how much oxy-

gen (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 percent of oxygen converted into water, (including the perhaps formed 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 18.

Comparison of Gas Conversion (Mixed Gas) With an Fe-Cu-MnO- and Cobalt-Manganese-(15%)-and-Cobalt-Thorium-(18%) Cat.[1]

	Fe-Cu-MnO + 1% K_2CO_3	Fe-Cu-MnO + 1% K_2CO_3	Cobalt-Manganese	Cobalt-Thorium
Temperature, °C.	220	220	195	190
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
Synthese (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, g./m³	50.0	49.0	98.7	94.5
Reaction water, ccm/m³ [2]	16	28	--	--

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

[2] Including the water of humidification of the not-dried starting gas. The water contents amounted 8 to 12 cc/m³.

The comparison of both contact species in Table 18 shows that the cobalt catalysts practically do not form any CO_2. Hence, they convert almost all the CO-oxygen into water. In contrast to the cobalt catalysts, the iron catalysts form a considerable part of CO_2. With them, only approximately half of the CO is used for the synthesis as such. Only approximately 16-12 percent of the CO-oxygen is converted into water when iron catalysts are used. By comparing column one with column 2, it may be observed that by reducing the gas rate down to 1/2, the water formation doubles approximately. The water formation increases from 16 to 28 cc. of water per m³ of gas. On account of the prevalent CO_2 formation, 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 will point this out: Referring to

Table 18, the mentioned cobalt-manganese catalyst acted on a mixed gas and gave 70 percent contraction. The reaction gas had the composition:

	CO_2	sKW	O_2	CO	H_2	CH_4-KW	C-Zahl	N_2
Percent	10.8	3.2	0.0	13.6	32.8	16.2	1.56	23.4

It is evident that the catalyst uses CO and H_2 approximately in the ratio of 1:2 that is, very close to the original ratio of the two gases in the mixed gas. The CO-H_2 ratio in the reaction gas is still 1:2.4. Theoretically, the possibility exists to remove the hydrocarbons from the reaction gas and obtain a 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 18 gave 30 percent contraction at 220°C., and a reaction gas of the following composition:

	CO_2	sKW	O_2	CO	H_2	CH_4-KW	C-Zahl	N_2
Percent	21.8	0.7	0.3	3.2	58.8	5.4	1.72	9.8

Here, 93 percent of the CO 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 used up 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 during 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 19, No. 2), the following end-gas analysis was obtained with 26 percent contraction:

	CO_2	sKW	O_2	CO	H_2	CH_4-KW	C-Zahl	N_2
Percent	18.2	0.3	0.2	9.0	59.8	2.5	2.75	10.0

The analysis shows that the shifting of the ratio of CO to 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 finally shows that the shifting of the ratio of CO to H_2 was already 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	sKW	O_2	CO	H_2	CH_4-KW	C-Zahl	N_2
Percent	8.1	0.0	0.4	21.4	60.1	2.8	1.43	7.2

Although only 26.5 percent of the CO was converted, the CO_2 to H_2 ratio in the reaction gas had shifted already 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 changes very rapidly all along the course of the reaction tube when iron catalysts are used. This is true even for very small contractions, and becomes more pronounced as the conversion increases. With an iron catalyst, therefore, only the first zones of the catalyst receive a gas of the original composition of CO to H_2. The following zones receive gases which are more and more enriched in H_2 and are leaner in CO. To convert such a gas to liquid products, obviously different reaction conditions are necessary than were required for the original gas.

Considering the comparatively high CO usage in connection 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 extremely fast when such a gas is used. The activity cannot be maintained even when the gas rate is reduced. Already when water-gas is employed, this rapid decrease of activity with the iron catalysts is noticeable. The mentioned shifting of the CO to H_2 ratio in the gas in connection with iron catalysts is the reason for not resorting to recycling in order to obtain a higher yield of liquid products and a more complete conversion.

In the following, a summary of the reaction gas analyses is given as it is obtained with an iron-copper-manganese catalyst at a temperature of 190 to 230°C. In order to facilitate working at a temperature of 190°C., a larger catalyst quantity was used for this experiment. The catalyst used corresponded to 120 grams of Fe-Cu-MnO. The analyses show how comparatively independent of the reaction temperatures the final gases become richer in H_2 and CO.

Temp. °C.	Gas rate, liters/hr.	Contr., percent	CO_2	sKW	O_2	CO	H_2	CH_4-KW	C-Zahl	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	0.2	0.2	6.8	61.1	2.5	2.20	9.4
220	3.9	32	22.4	0.3	0.1	1.7	60.0	6.6	2.55	8.9
230	4.6	33	21.6	0.6	0.2	1.9	55.4	10.5	1.46	9.8

(Bahr) VIII. Experiments on Water Formation.

As is mentioned already in Section VII, the smaller yields obtained with iron catalysts as compared to cobalt catalysts are caused chiefly because the reaction yields considerable CO_2 and not water. It has already been pointed out that with iron catalysts under certain conditions the formation of water may be observed. We investigated this some more and in the following series of experiments, we have 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 to H_2 ratio) upon the CO_2 and water formation.
    2. The influence of alkali contents upon the CO_2 formation on the iron catalysts.

3. The CO_2 formation on the iron catalysts by using a CO_2 containing initial gas.

4. The CO_2-water formation on iron catalysts containing carriers.

1. **The Influence of Gas Composition (CO to H_2 ratio) Upon the CO_2 and Water Formation.**

During the following experiments, Fe-Cu-MnO (4:1:1 containing one percent K_2CO_3) catalysts were used. They were prepared by precipitation from the nitrates with sodium hydroxide. According to our experiences at that time, we have found this to be the most favorable way of preparation. The comparatively high alkali content of one percent had an advantageous effect on NaOH precipitated catalysts. Later on, however, we used catalysts which were precipitated with soda, and we found that these catalysts are still more favorable. These catalysts should only be weakly alkalised 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	sKW	O_2	CO	H_2	CH_4-KW	C-Zahl	N_2
Percent	2.2	0.0	0.0	30.6	58.1	1.5	—	7.6

The ratio of CO to H_2 was equal to 1:1.9. To start with, we investigated the influence of the experiment temperature on the course of the CO conversion in the mixed gas. In order to extend the experiments and to be able to vary the temperature and gas velocity in wide ranges, a comparatively large contact quantity (120 grams to 80 grams of iron) was used. The results of the experiments are given in Table 19. They are arranged in increasing reaction temperatures. The table shows, in the first place, that at low temperatures of 200-210°C., a comparatively large quantity of the CO remains unconverted. This is mainly caused by the fact that the iron catalysts in this range of temperature show only little activity. In addition to that, we want to point out that one cannot succeed according to our present experiences to get an iron catalyst started at 200 or 210°C. over a period of time of 30 to 60 hours. We found that the time of induction is longer than that. The catalysts are first allowed to act at 220-230°C., up to such a time that they give a contraction of 20 to 25 percent. Thereafter, the temperature is lowered. The table then shows how, with increasing reaction temperature, the quantity of CO converted to CO_2 decreases when compared to the CO required for the synthesis. At 200-210°C., approximately the same amount of CO is converted to CO_2 as is converted to hydrocarbons. At these temperatures, no water was formed yet. Practically all of the oxygen went 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 formation. In accordance with all that, an ever increasing quantity of water 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 bring out the influence of the flow velocity.

At 9.8 liters of gas per hour and 240°C., approximately 40 percent of CO went to CO₂, whereas 54 percent was used for the synthesis. At 1.6 liters of gas per hour, approximately 1/3 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. In spite of that, the yield of liquid products for both experiments was 50 respectively 49.5 g./m³ of gas.

Table 19.
Influence of Temperature Upon CO Conversion (Mixed Gas) With Fe-Cu-MnO Catalysts Containing One 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
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	0.6	0.7	6.0	9.9	20.8	14.7	24.7
Reaction water, cc/m³ [1]/	12.3	10.7	16.4	26.5	42.9	26.7	n.b.*
Liquid products, g./m³.	22.7	29.6	50.0	49.7	49.5	n.b.	n.b.
Calculated theoretical yield grams of hydrocarbons/m³	73.5	69.4	87.5	92	99.8	92.2	102.7
Reaction gas CH_4 contents, 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

[1]/ Including humidification water.

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); then 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 experiment temperatures of 200 to 210°C., comparatively larger quantities of products other than liquid are formed. At 200°C., they amount to approximately 51 grams and at 210°C., they amount to 40 g./m³. Since the reaction gas from these experiments contains a comparatively small amount of methane hydrocarbons, one is justified to assume that during the reaction larger paraffin quantities remained in the catalyst when the working temperature was lower. For the following experiments which were con-

*n.b. = not observed.

dusted between 220-240°C., we observed increasing amounts of methane hydrocarbons in the reaction gas. The carbon number of the hydrocarbons decreases with increasing temperature. The difference between the calculated yield and the experimental yield of liquid ef-liquid product yield obviously is caused here chiefly by the increased formation of gaseous hydrocarbons. The gaseous hydrocarbons may be gasol or methane. If experiments 3 and 5 are compared one with another, 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 methane hydrocarbons were formed as were 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 back to experiments 6 and 7 which are listed in the table. From them, the influence of the flow velocity upon the nature of the conversion at 240°C., may be observed. One recognizes that by reducing the hourly throughput from 9.8 to 1.6 liters, the contraction increases from 30 to 38 percent; and 60 percent of the CO is consumed during the synthesis. From this 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 already apparent from the gas analysis that for this slow gas throughput, a large amount of gaseous hydrocarbons had fromed (14.3 percent methane hydrocarbons).

From a further series of experiments, one can observe that for still lower experiment temperatures, the benzene formation on the iron catalyst proceeds predominantly over CO_2 formation. The results of the experiments are tabulated in Table 20. In order to be able to lower the experiment temperature considerably, we used for this experiment a Fe-Cu-MnO catalyst which contained 5 percent K_2CO_3 (90 grams, 60 grams of iron). We initiated the catalyst at 220°C., whereafter the temperature was lowered gradually-the lowest experiment temperature was 170°C. For this temperature and a gas rate of approximately one liter per hour, still a contraction of 11 percent was observed. On account of the low throughput, we decided not to make a yield determination, and we merely checked up on the nature of the end-gas.

Table 20
CO Conversion (Mixed Gas) on Fe-Cu-MnO + 5% K_2CO_3 at Low Temperatures

	1	2	3	4
Temperature, °C.	220	200	190	170
Hours of operation	41	48	140	185
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	0.4
percent to CO_2	89.0	75.2	88.0	38.6

Table 20 shows (as is apparent from earlier experiments already) that in the range of the low reaction temperatures, the reaction practically only proceeds over 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 could observe the formation of small water quantities. Originally, we were inclined to believe that the differences in the reaction mechanism between iron as compared to cobalt catalysts was mainly due to the higher reaction temperatures which the iron demands. The above described experiments point out, however, that the iron catalyst under investigation did not form increasing quantities of water when it was permitted to work in the reaction temperature range of the cobalt catalysts. In fact, we observed just the opposite, 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. We intended to find out whether the CO_2 formation could be suppressed by using a larger excess of H_2. The gas employed had a CO to H_2 ratio of 1:4.2. The theoretical yield of liquid products may be calculated to be 108 grams of hydrocarbons por cubic meter. The composition of the gas was as follows:

	CO_2	sKW	O_2	CO	H_2	CH_4-KW	C-Zahl	N_2
Percent	0.0	0.0	0.0	18.6	79.2	—	—	2.2

The catalyst quantity used was 60 grams which was equivalent to 40 grams of iron. The experimental results are arranged according to reaction temperatures in Table 21.

Table 21
CO Conversion When Using H_2-rich Gas $(CO-H_2 = 1:4.2)$ on Fe-Cu-MnO Catalysts Containing One Percent K_2CO_3

	1	2	3	4	5
Temperature, °C.	200	210	220	230	240
Hours of operation	593	473	353	113	287
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/m³ [1]	16.6	24.1	28.3	25.4	28.8
Liquid products, g./m³	16.2	35.1	35.9	29.9	29.3
Reported theoretical yield, g. CH_2/m³	42.6	55.5	56.5	54.0	56.0
Reaction gas: CH_4 contents, percent	3.5	2.2	1.3	2.6	1.9
Carbon number	1.0	2.27	2.08	1.65	1.89

[1] Including humidity.

In general, Table 21 shows that an H_2-rich gas does not give any more favorable results as far as the suppression of the CO_2 is concerned. By using an H_2-rich gas, the water formation seems to set in somewhat earlier. We could observe water already at 210 and 200°C. However, at higher temperatures, as for instance, 230 and 240°C., the reaction water predominantly proceeds the CO_2 formation. The comparison with Table 19 (mixed gas experiments) shows that an H_2-rich gas does not give any better results than does a mixed gas as far as water formation is concerned at higher temperatures. Some additional interesting information may be obtained by studying Table 21. It appears that a H_2-rich gas has a tendency to produce comparatively large quantities of gaseous hydrocarbons in addition to the usual liquid products. This 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 a H_2-rich gas, the degree of conversion of CO to liquid products is not essentially larger than the degree of conversion with mixed gas. With a mixed gas containing 30 percent of CO (compare Table 19) on the average, 50 grams of liquid products per cubic meter are obtained. If this figure is referred to CO_2, it corresponds 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 when referred to CO_2.

In general, we want to bring attention to 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 catalyst required a longer time of induction when used with H_2-rich gases as 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 one percent K_2CO_3 (8 grams of iron). We wanted to investigate how the gas composition shifts at elevated temperatures (up to 260°C.). We obtained the following picture, (Table 22). With increased temperature, the CO_2 contents diminished and for the maximum case (260°C.), it decreased down to 35 percent of the originally employed CO. At this point, 57 percent of the CO was used for the synthesis. Such and similar results were observed earlier with mixed gas at 240°C., when larger catalyst quantities were employed, (compare Table 19, Experiment 5).

Table 22.- CO Conversion with H_2-rich Gases (CO to H_2 = 1:4.2) On Fe-Cu-MnO Catalysts Containing 1% K_2CO_3, for a Temperature Range of 230-260°C.

	1	2	3	4
Temperature, °C.	230	240	250	260
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	SKW	O_2	CO	H_2	CH_4-KW	C-Zahl	N_2
Percent	0.0	0.0	0.3	10.4	88.3	--	--	1.0

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

The experiments carried out in this connection followed those described in Table 21, without timely interruption. The same catalyst was used without a previous regeneration. The catalyst (60 grams = 40 grams of iron) at this time had been in operation already for 980 hours. A decrease of its activity had not been observed up to this time.

By using the CO-deficient gas, the experimental results of Table 23 were obtained.

Table 23.
CO Conversion for a CO-deficient Gas (CO-H_2 = 1:8.5)
on Fe-Cu-MnO Catalysts Containing 1% K_2CO_3

	1	2
Temperature, °C.	220	220
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, g./m³	n.b.*	19.7
Reaction water, cc/m³	--	23.2

Table 23 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 went 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 methane hydrocarbons with a carbon number of 1.78. The obtained yield of approximately 20 grams of liquid products would correspond to a degree of liquefaction of 65 percent as referred to half of the CO quantity in the original gas. As already pointed out, 65-60 percent of the liquefaction was reached with the previously described H_2-rich gas. One can see, therefore, that even by using a large H_2 excess, it was not possible to exceed this degree of liquefaction.

*n.b. = not determined.

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 catalyst quantities (respectively smaller gas throughputs) and working at higher reaction temperatures or using a H$_2$-richer original gas, one succeeds in directing the reduction of CO partly over water formation (for a 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 which was converted into CO$_2$ and the CO which was converted into synthesis products was 1:2.3 for the most favorable case (Table 23, Experiment 2). An essential increase in the yield of liquid products was however not connected with the water formation. 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 1:0.5), 65 to 66 percent liquefaction was obtained referred to CO$_2$.

From the experiments reported here, one may conclude that the water formation obviously proceeds in a different manner than it does with cobalt catalysts. It does not show up before a certain dilution of the CO in the reaction gas has been reached. When H$_2$-rich gases are used, this conditions is already met in the range of low contractions - for mixed gas, the formation of reaction water (visible separation of water in the receiver) is generally observed when a contraction of 25 percent is reached. Obviously, the CO was converted in the first sections of the apparatus to such a degree that the following sections of the unit were practically charged with a H$_2$-rich gas. Such a gas, however, furnishes predominantly gaseous hydrocarbons for the temperatures in question. Therefore, the yield of liquid products does not increase essentially any longer with the water formation.

2. Influence of Alkali Contents Upon CO$_2$ Formation Using Iron Catalysts.

In order to acquire full activity, the carrier-free Fe-Cu-MnO catalysts need an activation with fixed alkali. This is contrary to experience with cobalt catalysts. It could be assumed that the different course of the reaction with the precipitated iron catalysts may be due to the alkali contents of the catalyst. (By different course of the reaction, CO$_2$ formation is meant). This may refer to the alkali (K$_2$CO$_3$) which was added subsequently to the catalyst or it may refer to the alkali residual alkali contents of the precipitated catalysts (such as Na$_2$CO$_3$). Even if the iron catalysts are washed thoroughly, considerably quantities of Na$_2$CO$_3$ remain in them.

In order to investigate this point, a number of Fe-Cu-MnO catalysts were prepared for which ammonium carbonate was used as a precipitant. The method of preparation and the general behavior of these little-active catalysts has been described in Section III. In the following, we only want to discuss whether such catalysts which are free of fixed alkali favor the formation of water. In Table 24, the nature of the gas conversion for two such ammonium carbonate catalysts is described. Two Fe-Cu-MnO (4:1:1) catalysts were subjected to investigation.

Table 24

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	89.8
percent to H_2O (diff.)	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 24 seem to point out that an immediate relationship between the alkali contents of the catalyst and the CO_2 formation during the synthesis does not exist. This seems to be obvious because the catalysts which were precipitated with ammonium carbonate and were free of alkali, produced predominantly CO_2. The catalyst used in the first column was an exception. This catalyst produced water already at a time 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 a conversion of the CO by using larger catalyst quantities and by decreasing the gas throughputs (Experiment 2). However, here also we observed the characteristic feature already met before with iron catalysts, namely, 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.

3. Experiments on the CO_2 Formation on Iron Catalysts When Using a CO_2 Containing CO_2-rich Starting Gas.

In the following, we attempted to suppress the formation of CO_2 on iron catalysts by adding a certain percentage of CO_2 to the starting gas. Thus, the possibility might exist to use CO for the synthesis proper. For those experiments, we employed Fe-Cu-MnO catalysts (10:2.5:2.5) which were precipitated with soda and which contained 0.1 percent K_2CO_3. The original analysis is given in Table 25; and the CO-H_2 ratio amounted to 1:1.8. This was somewhat too low. Of several experiments, which on the whole gave substantiating results, only two are discussed here.

Table 25.- Reaction Gas Analyses by Using a CO_2-rich Starting Gas

Exp.	Temp. °C.	Throughput l. per hr.	Contraction percent	Composition of the Reaction Gases, Percent							
				CO_2	sKW	O_2	CO	H_2	CH_4	C-Zahl	N_2
	Initial gas:			10.3	0.0	0.0	30.8	55.1	--	--	3.8
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	0.2	8.0	54.4	3.9	1.38	3.6

By comparing the two reaction gas analyses with the initial gas, one can say already qualitatively that the addition of CO_2 to the starting gas does not impede the CO_2 formation. In both cases, the enrichment in H_2 has occurred in the end-gas which we are already familiar with from using mixed gas as initial gas. The ratio of the residual CO and H_2 has shifted to 1:7.2 for Experiment 1, and for Experiment 2, to 1:6.8. It shows that for Experiment 1, at least, the CO_2 formation was not influenced by the CO_2 addition to the starting gas. Neither was more CO-oxygen converted to water than when working with mixed gas. No reduction of CO_2 formation from CO was observed. Experiment 2 shows somewhat more favorable results. The ratio of water to CO_2 was 1:2.4. No increase in the yield of liquid products was obtained during this experiment. 44.5 g./m³ were found. This corresponds to a degree of liquefaction of 55 percent by taking into consideration the somewhat low H_2 contents of the starting gas. The degree of liquefaction just mentioned was referred to 1/2 of the usable CO of the starting gas.

Table 26.- Course of the CO Conversion By Using a CO_2 Containing Starting Gas

	Experiment 1 (235°)	Experiment 2 (240°)
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
to H_2O (diff.)	10.1	24.1
$H_2O:CO_2$	1:7.2	1:2.4

4. The CO_2 and Water Formation on Iron Catalysts.

An essentially different result with respect to CO_2 and water formation is observed when the previously described carrier catalysts are used instead of the so-far investigated metal catalysts. We investigated carrier catalysts for which the kieselguhr was added immediately and which were precipitated with soda. We also investigated precipitated catalysts for which the carrier material (tonsil) was added after the precipitation.

Fe-Cu-MnO-kieselguhr catalysts.

A description of the method of the preparation and the behavior of the kiesel-
guhr precipitated catalysts containing various quantities of kieselguhr has
been presented in Section VI. In general, we limited ourselves to investigate
the influence of the kieselguhr addition upon the CO_2 and H_2O formation. When
a precipitated catalyst (Fe-Cu-MnO, 4:1:1) was taken into operation, precipi-
tated with soda, and contained 6 grams of kieselguhr, the water formation set
in simultaneously with the oil formation from the very beginning. The temper-
ature was 235°C., and the gas throughput was 4 liters of mixed gas per hour.
For the earlier metal catalysts as already described, the formation of water
could only be detected after higher percentages of contractions were observed.
The 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 reaction gas
had the following composition.

	CO_2	sKw	O_2	CO	H_2	CH_4	C-7.	N_2
Kieselguhr catalyst, 30% contraction	11.5	1.1	0.2	13.9	59.4	2.7	3.37	11.2
Metal catalyst, 32% contraction	17.9	1.3	0.1	5.0	59.5	4.8	1.32	11.4

For comparison, the kieselguhr catalyst was compared with a carrier-free pre-
cipitated metal catalyst (precipitated with soda). The comparison showed that
the kieselguhr catalysts, at approximately the same contraction, gave essen-
tially smaller quantities of CO_2. Furthermore, it appears that with the kiesel-
guhr catalysts, a larger proportion of the CO remained unconverted. The final
gas did not show such a pronounced shifting of the ratio of CO to H_2. As was
experienced with metal catalysts, the ratio was 1:4.3 for the kieselguhr cata-
lyst as compared to 1:11.9 for the metal catalyst.

A better insight in the various gas conversions for the two mentioned catalysts
may be obtained from Table 27.

Table 27.- 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
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
to H_2O (diff.)	11.9	14.0
$H_2O:CO_2$	1 : 6.4	1 : 3.7

A comparison between the two series of experiments brings out that the reaction on the kieselguhr catalyst has a tendency to proceed more over water formation. For a total of 66 percent conversion of the CO, the ratio of H_2O to CO_2 formed was 1:3.7. Whereas the metal catalyst, at 88 percent conversion of the CO, gave a ratio of 1:6.4, that is approximately 6 times as much oxygen went to CO_2 than did to H_2O.

We did not make a yield determination of liquid products for the experiments described above. From calculations, we could observe already that in spite of the increased water formation on the kieselguhr catalysts (on account of the lower gas conversion) an increase in yield did not occur when compared to metal catalysts.

Further experiments confirm 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 28 shows the results of two further experiments. One of the tests was conducted with a catalyst which was somewhat leaner in copper.

Table 28.
Gas Conversion (Mixed Gas) on Kieselguhr Precipitated Catalysts

	1 Fe-Cu-MnO 4 : 1 : 1 Kieselguhr / 1	2 Fe-Cu-MnO 4 : 0.2 : 1 Kieselguhr / 1
Temperature, $^{\circ}C$.	235	235
Liters per hour	4	4
Contraction, percent	32.4	29.2
Reaction gas, volume percent CO_2	14.4	7.6
sKW	0.8	0.0
O_2	0.2	0.0
CO	11.2	18.5
H_2	54.2	57.1
CH_4-KW	5.9	2.8
C-Zahl	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
to H_2O (difference)	24.5	24.7
$H_2O:CO_2$	1 : 2.3	1 : 1.3

With catalyst No. 1, a conversion of 76 percent of the CO was obtained, and only 2.3 times as much CO_2 was formed than water. With catalyst No. 2, only 1.3 times as much CO_2 was formed as water, however, at a total CO conversion of 56 percent.

At any rate, for these experiments the larger part of the CO-oxygen still went
to CO_2. Therefore, we investigated further how far the CO_2 formation may be
suppressed: First, by using catalyts of still higher kieselguhr contents, and
secondly, by lowering the reaction temperature.

The magnitude of the possible maximum conversion for these experiments has not
been estimated. The reason for this was that the kieselguhr-rich catalysts
took up a very large volume in the reaction tube, and thus, permitted only
small quantities of Fe-Cu-MnO to be contained in the tube. With the carrier-
free catalysts considerably larger metal quantities could be introduced into
the reaction tube. In Table 29, two catalysts which are richer in kieselguhr
and which were precipitated with Na_2CO_3 are mentioned. The first catalyst con-
tains 2 parts of kieselguhr per part of Fe-Cu-MnO, whereas the second contains
3 parts of kieselguhr per part of metal.

Table 29
Gas Conversion (Mixed Gas) on Kieselguhr-rich Fe-Cu-MnO Catalysts

	1	2
	Fe-Cu-MnO 3:0.75:0.75 / kieselguhr 2	Fe-Cu-MnO 8:2:2 / kieselguhr 3
Temperature, °C.	235	235
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	83.6	24.4
to H_2O (difference)	13.7	23.5
$H_2O:CO_2$	1 : 2.4	1 : 1.04

From Table 29, it may be seen that the investigated 1:2 kieselguhr catalyst did
not behave more favorably than the previously described 1:1 catalyst as far as
water formation was concerned. The H_2O to CO_2 ratio was 1:2.4. However, for
a 1:3 kieselguhr catalyst, we succeeded to reduce the CO_2 contents to such a
point that approximately equal amounts of CO-oxygen went to CO_2 and water re-
spectively.

A further increase in kieselguhr resulted in still less active catalysts which
have not been investigated very thoroughly.

Another factor which influences the water formation favorably is to allow the
kieselguhr catalyst to work at a lower experiment temperature. Just as we did
in earlier experiments for the metal catalysts, here again we employed larger
catalyst quantities, and used a catalyst tube of larger diameter when working
at lower temperatures. This was necessary in order to obtain a sufficient
degree of conversion for the lower reaction temperature. We used 16 grams of

equivalent catalyst of composition 1(Fe-Cu-MnO) + 1 kieselguhr. The catalyst
was precipitated with soda, taken into operation at 235°C., then gradually the
temperature was lowered to 200°C., step by step. Thus, we obtained the condi-
tions reported in Table 30.

Table 30

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
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
to H_2O (diff.)	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
sKW	0.9	0.6	0.8
O_2	0.0	0.0	0.0
CO	19.3	23.4	20.6
H_2	58.9	58.8	58.8
CH_4-KW.	1.8	1.0	n.b.*
C-Zahl	3.3	2.3	n.b.*
N_2	11.1	11.2	n.b.*
$CO:H_2$	1 : 3.2	1 : 2.5	1 : 2.8

Table 30 shows that for the temperatures in question (215-205°C.) comparatively
favorable results were obtained in so far as the CO-oxygen conversion was con-
cerned. For Experiment 1, approximately twice as much CO went to synthesis pro-
ducts than did to CO_2. For Experiment 2, almost 3 times as much was used up for
synthesis products than was converted into CO_2. The ratio of H_2O-oxygen to the
CO_2-oxygen lies somewhere between 1:2 and 1:1.2. It has to be mentioned, how-
ever, that at these low temperatures, only 40 to 50 percent of the total CO
entered the reaction. However, the possibility exists to re-use the end-gas
once more and lead it back over the catalyst. This can be done because the CO
to H_2 ratio in the reaction gas has not changed considerably. For the experi-
ments discussed, this ratio lies between 1:3 and 1:2.5.

The kieselguhr catalysts differ essentially from the metal 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 metal catalysts
(see Tables 19 and 20), we found that the water formation decreases as the re-
action temperatures increases. As the reaction temperature drops, the water
formation finally comes to an end. For lower temperatures, therefore, the CO_2
value became more and more pronounced when compared to the synthesis value.

* n.b. = not determined.

"3-Layer Experiment" With Iron-Kieselguhr Catalysts.

The previously mentioned experiments show that the CO contained in the mixed gas are comparatively incompletely converted when using kieselguhr catalysts. The degree of conversion depends on reaction conditions. The magnitude of conversion varied between 40 to 70 percent. This lower degree of conversion may be due to the fact that the kieselguhr catalysts were more dilute in iron, hence, for a certain catalyst quantity, smaller iron quantities were used than in the case of the metal catalysts. In a further series of experiments, we have attempted to increase the gas conversion in one single stage by simply using greater catalyst quantities. For this larger catalyst quantity, we employed longer catalyst layers (longer reaction tubes). The reaction tubes used were up to 60 cm. long. The catalyst tubes used so far, were only 30 cm. in length.

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

In the following an experiment is discussed for which 3 catalyst layers were used in series, each catalyst layer being richer in iron than the previous one. Table 31 gives information on the arrangement of the experiment. The total iron quantity was 14 grams. The first layer was composed of a catalyst having a composition of one metal to 3 kieselguhr, the second layer consisted of a catalyst of one metal to one kieselguhr, and the last layer contained no kieselguhr at all. It may be seen that the catalyst was arranged according to the countercurrent principle. The entering mixed gas thus was intended to first contact the iron-deficient catalyst and then proceed to the iron richer catalyst layers.

To start with, layer No. 1 was taken into operation at 235°C. up to such a time for which the contraction was 13 percent. Table 31 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 respectively was equal to 1:1.8. The CO to H_2 ratio shifted only moderately. It was 1:24 for the reaction gas. At this point, catalyst layer No. 2 was taken into operation. The second layer was contained in a glass tube of somewhat smaller diameter than the contact tube. The glass tube was open at both ends. After a total of 47 hours, the contraction then 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 it had become more unfavorable. The oxygen conversion also had shifted in the direction of an increased CO_2 formation. The H_2O to CO_2 ratio was now 1:6.4, and the CO to 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 7 percent. The other conversion data shifted in the manner indicated in Table 31. When the temperature of 235°C., was

reached again, catalyst layer No. 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 more water was formed, only CO_2. The $CO-H_2$ ratio in the end-gas shifted sharply towards 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 layer length in connection with kieselguhr catalysts. The reason for this was that the water formed on the following 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 each stage of operation. In the following investigation, we carried out such an experiment using tonsil as a carrier. The experiment was not successful, however.

Table 31
Three-Layer Experiment

	35 cm.	25 cm.		20 cm.
	Fe-Cu+MnO 1 2:0.5:0.5 kieselguhr 3	Fe-Cu+MnO 1 4:1:1 kieselguhr 1		Fe-Cu+MnO + 0.1% 8:2:2 K_2CO_3
Temperature, °C.	235	235	225	235
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	73-3/4
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	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
to H_2O (diff.)	10.2	10.1	12.4	0.2
$H_2O:CO_2$	1 : 2.4	1 : 6.4	1 : 3.7	1 : (400)
Reaction gas, vol. percent CO_2	5.5	14.8	10.3	17.2
sKW	0.9	0.7	0.8	0.6
O_2	0.0	0.1	0.1	0.0
CO	23.2	10.5	17.1	7.7
H_2	55.7	54.1	54.5	55.9
CH_4-KW	2.9	6.2	3.8	5.6
C-Zahl	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 and 2	Same at a 10° lower temperature	Layer 1, 2, and 3

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 plays an important role. In Table 32, the results are described with a number of Fe-Cu catalysts containing different amounts of tonsil. They were precipitated by soda from ferrous chloride 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 non-alkalized catalyst. The catalyst contained 5Fe to 1Cu. To this, 4 grams of tonsil were added for every 10 grams of iron. The activity as compared to the tonsil-free catalysts is approximately 25 to 30 percent lower. Otherwise the course of the reaction is the same, that is to say, the reaction proceeds over CO_2 formation. When the tonsil is added prior to precipitation, an almost entirely inactive catalyst results (Experiments 3 and 4). The alkalized catalyst is still less active than the non-alkalized catalyst. A reduction with H_2 at 450°C., does not change the situation. When the same tonsil quantity is added after the iron copper precipitation had taken place, a decrease in activity results here too but it is by far not as serious as when the tonsil is added prior to precipitation. Both catalysts, with and without alkali, reach a maximum contraction of 16 percent, and in this condition furnish 26 respectively 22 grams of liquid products per cubic meter of mixed gas. Water is formed simultaneously. Up to 20 g./m³ of mixed gas were obtained. A tonsil-free catalyst, under the same conditions of operation, yields no water at a contraction of 16 percent. It is evident, therefore, that for the tonsil-containing catalysts, the reaction proceeds partly over the formation of water just as in the case of the previously described kieselguhr catalysts. The CO_2 formation is suppressed and consequently more CO is available for the formation of hydrocarbons.

(Table 32, next page)

This is apparent by comparing the end-gas analyses for tonsil-containing and tonsil-free catalysts at approximately the same contraction (Table 33). The tonsil-containing catalysts for the same contraction form only approximately half the CO_2 quantity. Correspondingly, the CO contents in the end-gas is higher than in the case of the tonsil-free catalysts. Normally, using carrier-free iron catalysts, each mole of CO which is used up for the hydrocarbon synthesis should also form one mole of CO_2. 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 proceded to 1/2 over the formation of water and the other half to the formation of CO_2.

Table 32

Influence of Tonsil Addition to 5Fe-10u Catalyst

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

Table 33
Influence of the Tonsil Upon the End-Gas Composition.

Catalyst 5Fe-10Cu	Contraction, percent	End-gas Composition							
		CO_2	sKW	O_2	CO	H_2	KW	C-Zahl	N_2
Contains tonsil + 1/4% K_2CO_3	15.5	4.9	0.4	0.2	24.8	57.8	2.1	1.76	9.8
"	16.0	5.4	0.6	0.1	23.0	58.9	2.1	2.0	9.9
Contains tonsil without K_2CO_3	16.0	5.2	0.6	0.1	23.3	58.9	2.6	1.85	9.9
Without tonsil, 1/4% K_2CO_3	15.5	9.9	0.9	0.1	17.1	59.6	1.7	1.4	10.7
"	15.0	9.0	0.4	0.1	17.6	60.6	1.5	1.67	10.8

Next we tried to obtain a better degree of conversion by raising the reaction temperature. We regret to state that increasing the temperature by 15°C. (from 235 to 250°C.), the contraction only increased to 20 percent. The CO_2 contents, however, went up from 4.9 to 8.6 percent, and the water formation ceased almost entirely. We are forced, therefore, to assume that at higher temperatures, the primary water reacts with the secondary CO under CO_2 formation. By decreasing the flow velocity from 4 to 1 liter per hour (Experiments 5 and 6, Table 32), a significantly higher conversion was obtained. We observed that the contraction increased from 16 to 32 percent respectively 29 percent. The water formation, however, decreased very considerably; whereas the CO_2 contents 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 respectively 35 grams although 85 percent of the CO was converted.

Therefore, it is apparent that neither by raising the temperature nor by decreasing the flow velocity are we in a position to cause a reaction to take place in the desire manner. We tried one further arrangement which was generally recognized as favoring water formation, namely multi-stage operation in series. The experiment temperature was 235°C., and the flow velocity, 4 liters per hour. The end-gas of the first stage after removing the liquid reaction products was recirculated. In this manner, 90 percent of the CO was worked up in 4 stages. The total contraction amounted to 40 percent (See Table 34), 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 contents of gaseous hydrocarbons in the end-gas. It has to be taken into consideration that part of the gas is removed by the activated charcoal behind the individual stages. A CO balance gives the following picture: Of the total CO converted (90 percent) 40 percent went to CO_2 and 60

percent was converted to hydrocarbons. The ratio of CO_2 to hydrocarbons is, therefore, 2:3. From the CO quantity which was used up for the synthesis, theoretically 100 grams of liquid products could be obtained. Since in reality only 48 grams of liquid products were obtained, the portion of the CO which went to gaseous hydrocarbons amounted to 50 percent.

Table 34.
Four-Stage Experiment with Tonsil-Containing Catalyst

Stage	Contraction, percent	Grams of liquid products per m^3 of mixed gas	Gas composition							
			CO_2	sKW	O_2	CO	H_2	KW	C-Zahl	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	0.3	0.3	17.1	56.0	4.0	1.88	11.8
3	10.0	8	15.6	0.0	0.0	9.8	55.4	5.8	1.76	13.4
4	6.3	4	19.5	0.1	0.3	5.2	54.9	6.0	1.83	14.0
1 - 4	40.3	48								

In conclusion, we should like to give some of our speculations on why we believe that carrier catalysts are capable of forming water and why metal 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 phenomena 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, however, as pointed out in Section XIV, not reduced on the iron catalyst at the temperature range in question. With the carrier catalysts, however, according to observations from the experiments, this subsequent CO conversion by the reaction water takes part only to some extent. It may be that the reason for this behavior is in the dilution of the catalyst and in the fact that the temperatures at the various active centers are not quite as high as they are in the case of metal catalysts. The metal catalysts, on account of their concentrated form, develop more heat per unit volume, whereas the carrier catalysts develop less heat for the same volume on account of the carrier dilution.

IX. Best Catalyst Obtained.

Of the iron catalysts described in Sections III and IV, the best catalyst found, especially with respect to stability, was a 5Fe-1Cu containing 1/8 percent K_2CO_3. Its method of preparation is as follows: 180 grams of $FeCl_2 + 4H_2O$ (50 g. of Fe) and 26 grams of $CuCl_2 + 2H_2O$ (10 g. of copper) are dissolved in one liter of water. The chloride solution is heated to the boiling point and precipitated with a solution containing 160 grams of soda in 1-1/2 liters of water (time for precipitation, 1/12 to one minute). The precipitate is filtered and washed 6 times with one liter of hot water each. After drying at $105°C$., the catalyst mass is powdered and impregnated with 67-1/2 mg. of K_2CO_3 (1/8 percent referred to iron). The K_2CO_3 was dissolved in 100 cc. of water. The impregnated mass is 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 of the precipitate into the still moist and not previously dried catalyst mass.

A catalyst mass which contained 10 grams of iron was taken into operation immediately and without any previous pretreatment. The gas used was mixed gas (29CO - 58 H_2), and the flow velocity was 4 liters per hour at a temperature of 235°C. The maximum contraction was 31 percent, and was already reached after 2 days of operation. After lowering the temperature 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 g./m³ of mixed gas. For 7 weeks of operation, it was 50 g./m³ of mixed gas, and for 8 weeks, it was still 47 g./m³ of mixed gas.

From Table 35 (see also curve __?__) the behavior of such a catalyst may be observed for 8 weeks of uninterrupted operation. The experiment temperature was raised by approximately 10 degrees 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 7 weeks of operation, the experiment 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 yield: contraction had increased from 1.52 to 1.66.

Table 35
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
Experiment Temperature, °C.	230	228	229	230	233	233	237	230
Contraction, percent	30	30	30	30	28	26	25	15
Yield in g./m³ of mixed gas	56	55	56	52	47	45	38	25
Average yield in g./m³ of mixed gas	56	56	56	55	53	52	50	47
$\dfrac{\text{Yield}}{\text{contraction}}$	1.87	1.04	1.87	1.73	1.68	1.72	1.52	1.66

In some cases catalysts were obtained with the above mentioned method of preparation which gave a maximum yield of 60 grams of liquid products per cubic meter of mixed gas. For the above described experiment with a maximum yield of 56 grams of liquid products, a catalyst was used the activity of which may be surpassed in some instances.

X. Regeneration of the 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 in order 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. A preceding extraction with benzene is recommended in order to recover the high boiling accumulated paraffin hydrocarbons which are always present in the catalyst.

Table 36
5Fe - 1Cu Catalyst + 1/4 Percent K₂CO₃
Regeneration Under Various Conditions

Mode of regeneration	Extracted paraffin in grams	Yields in g./m³ after days				
		6	17	24	32	39
1. H₂ treatment at 235°C., benzene extraction, then treatment with air at 235°C.	7.2	55	53	50	43	37
2. Benzene extraction, then air treatment at 235°C.	9.0	53	50	48 after28	44 36	35 43 days
3. Air treatment at 235°C. only.	-	55	52	49	48	43

Table 36 shows the course of the second operation period, when using a 5Fe-1Cu catalyst containing 1/4 percent K₂CO₃ 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 g./m³ of mixed gas (average yield for 6 weeks operation, 49 grams uncorrected.). Catalyst 1 was, at first, treated with H₂ at 235°C., then extracted with synthetic benzene (boiling point 80 to 100°C.), and finally oxidized with air. Catalyst 2 was extracted with benzene and then oxidized with air; whereas catalyst 3 was merely oxidized with air.

For all three catalysts, after the regeneration under varying conditions, practically the original maximum yields could be obtained again. Catalyst 3 is even superior to both the other catalysts in so far as stability is concerned. Whereas for catalysts 1 and 2, after removal of the paraffin, a 24-hour oxidation with air was sufficient, the 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 paraffins, respectively acids.

It should be mentioned here that a 5Fe-1Cu catalyst containing 1/4 percent K₂CO₃ and formed with starch reached its original activity after a paraffin extraction with benzene and a subsequent oxidation with air had been performed. 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. We want to mention here that no reactivation is possible by merely conducting H₂ respectively H₂-NH₃ mixtures over the iron catalysts. When the catalyst was treated with H₂-NH₃ mixtures, a small degree of reactivation is obtained; it is, however, of short duration only.

The 5Fe-10u catalysts which contained only 1/8 percent K_2CO_3 could be extracted with benzene and could subsequently be oxidised in a stream of air, so as to regain their activity completely. When the catalysts contained only 1/16 percent K_2CO_3, by regeneration, an initial yield of 51 grams was obtained also; 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 which was 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. It should be mentioned here that an extraction alone without subsequent oxidation only causes an 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.

A 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 respectively 1/2 percent K_2CO_3 alkali (they gave a maximum yield of 45 grams respectively 47 grams of liquid products) after being treated with air after 8 days of operation gave only a contraction of 13 respectively 3.6 percent. During the first two days of operation, these catalysts had already given a contraction of 20 respectively 23 percent.

Meyer) XI. Regeneration of the Exit Gases.

In Section VII, we have mentioned a disadvantage which occurs when the benzene synthesis is carried out on iron catalysts by using mixed gas of composition $1CO + 2H_2$. The disadvantage cited is that an approximately equal quantity of CO is used up for the formation of hydrocarbons and for the formation of CO_2. This conversion to CO_2 is responsible to a great degree for the comparatively small yield of approximately 60 grams of liquid products per cubic meter of mixed gas. The degree of liquefaction by which we understand 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 grams per cubic meter. A further increase of the degree of liquefaction at the expense of the already small quantities of gaseous products formed appears therefore barely possible, since we do not succeed well to direct the reaction over the course of water formation when iron is used instead of cobalt. In some cases, it appears purposeful to reconvert the exit gas obtained during the benzene synthesis into synthesis gas. This is to be recommended especially 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.

    a. Use of Coke at High Temperature.
    b. Use of Coke at High Temperature, and in Presence of Illuminating Gas.
    c. Use of Coke at High Temperatures in Presence of Broken Clay.

(a) The exit gas was conducted over a layer of coke 10 cm. in length. The coke was granular in shape and was approximately of pea-size. It was contained in a porcelain tube of 16 mm. I.D., and the temperature under which the gas was conducted over the coke was 1000°C. In order to protect the reaction gas from later changes which might occur when the reaction gas comes in contact with regions of lower temperature, it was conducted away from the hot zone as rapidly as possible by using a 2 mm. wide porcelain capillary. The heating of the porcelain tube was accomplished in a Mars furnace.

In Table 37, the composition of the reaction gases is tabulated for various regeneration temperatures.

Table 37.
Conversion of the Reaction Gas on Coke at High Temperatures.

Temperature, °C.	CO_2	sKW	O_2	CO	H_2	KW	C-Zahl	N_2	Expansion, percent
Final gas from the benzene synthesis.	20.5	0.5	0.0	4.0	60.5	3.2	1.2	11.7	-
At 1030°	2.7	0.2	0.0	31.0	53.7	2.0	1.0	10.0	10
At 1100°	1.8	0.2	0.0	33.4	53.9	0.7	1.0	10.0	19
At 1150°	0.6	0.1	0.0	34.8	54.7	0.5	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 has participated in the reaction furnishes the gas expansion experienced during the conversion. This expansion amounted to 23 percent at 1150°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.

(b) In order to arrive at a CO-leaner respectively H_2-richer synthesis gas, various quantities of city gas were mixed to the exit gas obtained from the benzene synthesis. The mixture thus obtained was conducted over coke at 1100°C. Table 38 shows experimental results of this regeneration.

Table 38.
Conversion of the Reaction Gas on Coke in the Presence of City Gas at 1100°C.

Added quantity of illuminating gas, percent	CO_2	sKW	O_2	CO	H_2	KW	C-Zahl	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	0.0	31.6	57.1	1.6	1.0	8.7
20.5	0.7	0.0	0.0	31.4	57.6	1.3	1.0	9.0
23.0	0.5	0.1	0.2	30.8	57.6	1.2	1.0	9.6
26.0	0.9	0.0	0.1	29.3	58.3	1.6	1.0	9.8
28.5	0.8	0.0	0.2	28.6	59.1	1.6	1.0	9.7
Composition of the exit gas from the benzene synthesis	21.8	0.1	0.0	4.4	58.6	3.2	1.13	11.9

With an addition of 26 respectively 28.5 percent illuminating gas to the exit gas
obtained from the benzene 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, however, is not to indicate that
for all exit gases obtained from iron catalysts, the situation is as described
for the synthesis. So, for example, we found that for a CO_2-leaner end-gas con-
taining only 19 percent CO_2 and 61.8 percent H_2, the addition of 18 percent il-
luminating gas was sufficient to arrive at a synthesis gas containing 28.3 per-
cent CO and 58.4 percent H_2. The gas expansion experienced in this conversion
(the conversion of end-gas to synthesis gas) amounted to 17-20 percent.

(c) A third possibility to regenerate the exit gas obtained from the ben-
zene synthesis consists in heating the gas to very high temperatures in the
presence of ceramic material. Table 39 summarizes the reaction gas analysis
after the end-gas was conducted over broken clay at various temperatures.

Table 39.
Conversion of the Reaction Gas on Broken Clay.

Temperature, °C.	CO_2	sKW	O_2	CO	H_2	KW	C-Zahl	N_2
Composition of the exit gas from the benzene synthesis	17.8	1.0	0.1	5.2	62.3	2.6	1.31	11.0
1000°	9.6	0.0	0.0	18.1	57.9	3.0	1.0	11.2
1100°	4.7	0.0	0.3	23.9	56.6	2.9	1.0	11.7
1200°	2.5	0.0	0.1	26.6	57.3	2.2	1.0	11.3
1230°	1.8	0.0	0.3	27.2	57.6	1.9	1.0	11.5
1300°	1.6	0.0	0.0	28.1	58.4	0.8	1.0	11.1

As is noticeable from the table, a reaction temperature of 1200°C. is required
if it is desired to produce a synthesis gas containing 2.5 percent CO_2, 26.6 per-
cent 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, which to a certain extent is com-
pensated by expansion reactions of the hydrocarbons. In the best instance, a max-
imum contraction of 8 percent was ascertained.

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.

(Meyer) XII. Two-stage Experiments with Water Gas and Mixed Gas on Iron-Copper Catalysts.

a. Water-Gas Experiment.

As has already been pointed out in Section IX, a catalyst composed of 5Fe-1Cu con-
taining 1/4 percent K_2CO_3 (precipitated from $FeCl_2$ and $CuCl_2$ and by using Na_2CO_3 as
precipitant) will give 50 grams of liquid products per cubic meter of mixed gas
when permitted to act on mixed gas of composition 29 percent CO and 50 percent H_2.
This was found to hold for 6 weeks of operation during which time no regeneration
of the catalyst was required. Since during this experiment the synthesis gas is

depleted in CO quite considerably and since only moderate quantities of gaseous hydrocarbons are 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 tried to employ water gas instead of mixed gas. We worked in two stages using iron catalysts of the same composition in both stages. The object was to increase the yield per cubic meter of synthesis gas. To start with, we attempted to find the highest possible yield and the stability of the iron catalyst. The result of this investigation is given in Table 40.

Table 40

Maximum Yields and Stability of the Fe-1Cu Catalyst Containing 1/4 Percent K_2CO_3 When Water Gas Is Used

Days of operation	Experiment Temperature, °C.	Contraction, percent	Yield in grams of liquid products/m³ of water gas
6	253	40	75
10	237	35	67
14	237	29	53

With an initial maximum yield of 75 grams per cubic meter, the effectiveness of the catalysts decreases rapidly as compared to the operation for which mixed gas was used. After 14 days of operation, the quantity of liquid hydrocarbons formed had already decreased to 53 g./m³. Aside from the actual decrease in yield, the deterioration of the catalyst in this case is already noticeable from the early appearance of yellow-colored reaction products. As compared to the water gas experiment, the yellow-colored products appear much later when mixed gas is employed. With mixed gas, we could operate for 4 to 5 weeks before the colored product was noticeable. Here again, we had the old experience, namely, that a catalyst loses its activity approximately at the same rate at which the yellow products are formed which we believe to be paraffin decomposition products. It should be 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 worked in two stages. Two tubes, each containing 10 grams of iron, were operated in series and 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 was passed on over the second catalyst without removal of the CO_2. The results of this experiment are summarized in Table 41. 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 were obtained. In spite of the higher yields, the decrease in activity is not quite as pronounced as when water gas was used in a one-stage operation. One should keep in mind, however, that during the two-stage experiment, twice the catalyst quantity was used.

Table 41.

Two-Stage Experiment with Water Gas on a 5Fe-1Cu Catalyst Containing 1/4% K₂CO₃

Days of operation	First stage			Second stage		Sum of liquid products collected in 1st. and 2nd. stage
	Temp., °C.	Contraction, percent	Liquid products, g/m³	Contraction, percent	Liquid products, g/m³	
7	230	30	55	20	30	85
12	232	27	52	18	28	80
18	230	20	42	18	27	70

It is our belief that if we should increase the flow velocity from 4 to 8 liters per hour, corresponding to twice the catalyst quantity, the results obtained with the two-stage experiment should be less favorable. However, we have not carried out this experiment. The reason for not having investigated this was that 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 of the activity in the first stage when using water-gas should be blamed on the higher CO concentration which the water-gas has. If the flow velocity should be doubled, this disadvantage would become even more pronounced than with a corresponding increase in flow velocity when mixed gas is used. In the later 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 has already decreased to 46 grams.

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

b. Two-stage experiment with mixed gas without regeneration of the 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 benzene had been removed appeared not very promising to us. The reason for this is that the CO is already converted rather completely after one single stage. It is to be noted that gaseous products appear only in small quantities. In fact, when we did carry out a two-stage experiment for which we worked with twice the flow velocity, namely 8 liters per hour, corresponding to twice the catalyst quantity, no improvement in the yield of liquid hydrocarbons was observed.

Two-stage Experiment with Mixed Gas with Regeneration of the 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 of the benzene, and then passed over pieces of clay at 1200°C. This operation regenerated the gas and made it over to synthesis gas. It was carried 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 K₂CO₃. The flow velocity was 3 x 4 liters per hour, in other words, 12 liters of mixed gas per hour. The reaction gas was denuded of liquid reaction products and continuously regenerated on

pieces of clay by passing it through a Mars furnace at 1200°C. The synthesis gas thus formed was immediately conducted into the second stage. In accord with the contraction in the first stage and the gas volume reduction resulting from passing through the Mars furnace (from 12 to 8 liters per hour, the second stage was only charged with 2 parts of iron catalysts. Table 42 contains the results of this experiment.

Table 42

Two-stage Experiment with Mixed-Gas Regeneration of the End-Gas from the First Stage

	Temp., °C.	Contraction, percent	Grams of liquid products per cubic meter of mixed gas
1st Stage	230	30	56
2nd Stage	230	26	37
1st and 2nd Stage	-	approximately 50% referred to starting gas.	93

Table 43

Composition of the Starting Gas and Reaction Gas for Both Stages

	CO_2	sKW	O_2	CO	H_2	KW	C-Zahl	N_2	Residual gas quantities still present from 1000 liters
Starting gas, first stage	1.0	0.0	0.0	29.6	59.5	1.8	1.0	8.1	1000
End-gas, first stage	19.9	0.1	0.3	3.9	59.9	5.6	1.21	11.2	700
Regenerated end-gas	2.4	0.0	0.2	26.3	56.9	3.0	1.0	11.2	680
End-gas, second stage	19.8	0.9	0.2	2.5	58.6	4.9	1.5	14.9	500

It is possible therefore to obtain 93 grams of liquid products from one cubic meter of mixed gas. 56 grams of the 93 grams were obtained in the first stage, and the residual 37 grams from the second stage. However, it was required that the gas was regenerated after the first stage before it was admitted into the second stage. Referring the yield to normal conditions, the number increases from 93 to 102 grams per cubic meter of mixed gas. From the last column of Table 43, it is seen that from originally 1000 liters of mixed gas employed, 500 liters were still present leaving the second stage. After another regeneration of this end-gas, 25 grams additional liquid hydrocarbons could be obtained; so with a 3-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 it is to be recommended to pass the synthesis end-gas through the generator during the gas production period. A two-stage operation with water-gas for which the end-gas is regenerated after having passed the first stage, gives a higher yield for the first days of operation as compared to mixed gas. The yield with water gas amounted to 70 grams for the first stage, and 33 grams for the second, a total therefore of 103 grams (uncorrected). The activity of the iron catalyst, however, decreases more rapidly with the use of water-gas. This holds especially for the second stage. The reason is that the end-gas contains more CO than H_2 after it has gone through the broken clay and was regenerated at 1200°C. For example, its CO content was 44 percent and H_2 content only 32 percent.

d. Two-stage experiment with water-gas.

1st Stage: Fe catalyst.
2nd Stage: Co catalyst.

Finally we want to give the results of a two-stage experiment for 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 sufficient CO during the first stage containing the iron catalyst, so that the end-gas from the first stage had approximately the composition, $1CO + 2H_2$. A gas of such a composition is most favorable for the execution of the benzene synthesis on cobalt catalysts. In this manner, benzene may be easily obtained in places where the local conditions provide sufficiently cheap water-gas. The results of such an experiment are summarized in Table 44. Benzene and oil were removed after the first stage. The CO_2 formed was not scrubbed out.

Table 44.

Two-Stage Experiment With Water-Gas

(1st Stage Fe catalyst) 10 g. Fe
(2nd Stage Co + 18% ThO_2) 4 g. Co

Stage	Temp., °C.	Contraction, percent	Liquid products g./m³
1st Stage (Fe)	224	21	35
2nd Stage (Co)	130	64	68
1st and 2nd Stage			103
1st Stage (Fe)	228	27	47
2nd Stage (Co)	180	57	68
1st and 2nd Stage			115

Table 45

Composition of the Reaction Gas Behind the Various Stages

	CO_2	sKW	O_2	CO	H_2	KW	C-Zahl	N_2
End gas 1st Stage	14.7	0.5	0.0	28.5	46.6	1.2	1.75	8.5
End gas 2nd Stage	35.7	1.7	0.1	25.6	13.9	6.0	1.74	17.0
End gas 1st Stage	20.1	1.1	0.1	23.3	44.2	2.2	1.77	8.9
End gas 2nd Stage	46.4	1.5	0.3	8.9	15.2	10.3	1.82	17.4

The first row shows that the first stage gives 35 grams of liquid products at a
contraction of 21 percent (iron catalyst). The end-gas analysis (Table 45) shows
however, that the gas composition $1CO + 2H_2$ has not been reached yet, instead
CO is still present in excess. With this end-gas, a yield of 68 grams was ob-
tained in the second stage using a cobalt catalyst. The CO_2 was not previously
removed, and the contraction was 64 percent (Table 45, 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 that an ex-
cess CO was present as far as the cobalt catalyst was concerned. During a
second experiment, therefore, we charged the Fe catalyst stage somewhat more
heavily. One can see that with a contraction of 27 percent (row 3), the yield
amounts to 47 grams, and that the end-gas approximately corresponds to a $1CO +$
$2H_2$. This end-gas furnished 68 grams of liquid products per cubic meter of
water gas when going through 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 contains CO and H_2 in approximately the ratio of 1:2 which
is proof of the fact that the gas used for charging the second stage corres-
ponded nearly 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 oc-
curred, 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 was observed to have formed. The CO_2 which was obtained in the first stage
and which entered the second stage was apparently not attacked while going
through the second stage. We believe this to be true because it appeared that
the CO_2 quantity after the second stage was equal to that after the first
stage. Furthermore, if the CO_2 would have 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
in Section XIV. It is apparent from the experiments that with mixed gas, ad-
vantages result in a multi-stage operation only then 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.

Meyer)

XIII. Significance of the Iron Catalysts for the Simultaneous Production of CO-Deficient City-Gas and Benzine in Connection with Gas Works.

Considering the byproduct coke which is 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 benzene. For this purpose, the water-gas produced has to be processed first to a greater or lesser extent and the CO_2 formed has to be removed.

From the H_2-rich synthesis gas thus produced, containing for example, 20 parts of CO and 70 parts of H_2, by means of cobalt catalysts under proper reaction conditions, approximately 50 g./m^3 of liquid products may be obtained, and the end-gas from the synthesis, which is lean in CO, conforms closely to the specifications of a standard city gas.

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

Table 46.

End-Gas with Fe Catalysts for Gases of Various CO Contents

Temp., °C.	Days of operation	Contraction, percent	Grams of liquid products per cubic meter of gas	End-gas composition							
				CO_2	sKW	O_2	CO	H_2	KW	C-Zahl	N_2
1a **Synthesis Gas: 20CO-75H₂**											
226	-	27	47	10.2	0.5	0.0	1.8	80.5	2.1	1.67	4.2
After removal of CO_2				—	0.6	0.0	2.0	90.4	2.3	1.67	4.7
1b **Synthesis Gas: 29CO-58H₂**											
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	0.0	5.0	74.4	5.5	1.68	13.4
230	15	31	56	19.7	0.9	0.0	3.5	61.3	4.3	1.63	10.3
After removal of CO_2				—	1.1	0.0	4.4	76.6	5.4	1.63	12.5

Table 46 gives some end-gas analyses which were obtained when various starting gases were used with Fe-1Cu catalysts containing 1/4 percent K_2CO_3 (precipitated from $FeCl_2$, $CuCl_2$, and soda). 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, of the indicated composition. 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 47.)

Table 47
End-Gases with Fe Catalysts and Mixed-Gas at Elevated Temperatures

Starting gas	Temp., °C.	Days of operation	Contraction, percent	Grams of liquid products, gas	CO₂	sKW	O₂	CO	H₂	KW	C-Zahl	N₂
1. 29 CO - 58 H₂	230	6	30	53	19.3	0.5	0.2	3.4	61.8	3.3	1.8	11.5
After removal of CO₂					—	0.6	0.3	4.2	76.5	4.1	1.5	14.3
2. 29 CO - 58 H₂	245	7	33	—	20.0	1.5	0.3	1.7	57.5	6.4	1.5	12.6
After removal of CO₂					—	1.9	0.4	2.1	71.9	3.0	1.5	15.7
3. 29 CO - 58 H₂	245	11	28	—	19.2	1.2	0.3	4.0	59.1	4.4	1.4	11.8
After removal of CO₂					—	1.5	0.4	5.0	73.1	5.4	1.4	14.6
4. 29 CO - 58 H₂	270	12	34	—	20.2	1.9	0.4	1.8	56.0	7.0	1.27	12.7
After removal of CO₂					—	2.4	0.5	2.3	70.0	8.8	1.27	16.0
5. 29 CO - 58 H₂	270	14	26	—	17.2	1.4	0.2	4.8	60.0	5.1	1.25	11.3
After removal of CO₂					—	1.7	0.2	5.8	72.5	6.2	1.23	13.6
6. 29 CO - 58 H₂	300	14	34	—	19.2	2.3	0.0	3.5	54.5	8.1	1.26	12.4
After removal of CO₂					—	2.8	0.0	4.3	67.5	10.0	1.26	15.4
7. 29 CO - 58 H₂	300	15	11.5	—	9.7	0.9	0.2	17.4	59.1	3.1	1.07	9.6
After removal of CO₂					—	1.0	0.2	19.3	65.5	3.4	1.07	10.6

On account of the higher experiment temperatures, the activity of the catalyst decreases rapidly with a simultaneous formation of yellowish-colored products. After 4 days of operation, starting from the moment when the temperature was raised to 245°C., the contraction decreased from 33 to 28 percent. The end-gas has a composition as given in row 3. The quantity of the gaseous hydrocarbons formed, therefore, has decreased and is approximately of the same order of magnitude as that of an iron catalyst operated at 230°C. A further increase in the reaction temperature to 270°C., causes the contraction to go up again as well as the formation of the gaseous hydrocarbons (column 4). It is apparent from the low carbon numbers that primarily CH_4 was formed. After 2 further days of opera-

tion, the contraction had decreased from 34 to 26 percent; Correspondingly, the quantity of gaseous hydrocarbons decreased (column 5). We also made an experiment for which we worked at 300°C. Referred to CO_2-free gas initially 10 percent of gaseous hydrocarbons were formed. Already after 24 hours, the contraction had decreased to 11.5 percent, and only 1.4 percent of saturated gaseous hydrocarbons were observed.

Table 48
End-Gases with Fe-Catalysts and Water-Gas

Starting gas	Temp., °C.	Days of opera- tion	Con- trac- tion, percent	Grams of liquid products, m³ gas	CO_2	sKW	O_2	CO	H_2	KW	C- Zahl	N_2
1. Water gas 44 CO-47 H_2	236	6	40	75	36.1	2.3	0.2	6.1	41.5	4.2	1.88	9.6
After removal of CO_2					—	3.6	0.3	9.5	65.0	6.6	1.88	15.0
2. Water gas 44 CO-47 H_2	236	10	36	67	30.5	2.8	0.3	11.0	40.8	4.8	1.6	9.8
After removal of CO_2					—	4.0	0.4	15.8	58.9	6.9	1.6	14.1

Table 48 reports the composition of two end-gases which were obtained with water-gas acting on an iron catalyst. An essential increase of the gaseous hydrocarbons as compared to the mixed-gas experiments has not taken place. Experiments at elevated temperatures were not carried out. The reason for not investigating higher temperatures was that iron catalysts lose their activity considerably faster when water-gas is employed than when mixed-gas is used. This even holds for low temperature regions for which chiefly liquid products are formed. An increase in temperature therefore and using water-gas with iron catalysts would certainly have a tendency to decrease the lifetime of the iron catalysts still more than in the case of mixed gas.

Summarily, we can say that the reaction gases obtained from the benzene synthesis when using iron catalysts do not possess the proper requirements of a good city gas. The contents of gaseous hydrocarbons in the exit gas are too low, and the required heating value thus is not assured. The different composition of the end-gases obtained with iron catalysts as compared to the composition of end-gases obtained with cobalt catalysts may be explained by the different course of the reaction which takes place respectively on iron or cobalt. Since, on account of the CO_2 formation, only approximately half of the CO in the synthesis gas is converted into hydrocarbons when iron is used, the amount of gaseous hydrocarbons left in the exit gas is considerably lower than when cobalt is used. Furthermore with cobalt catalysts, a considerable increase in gaseous hydrocarbon contents occurs due to the high contraction which is caused by the water formation. This is not the case with iron catalysts because chiefly CO_2 is formed which does not reduce the contraction as much as the condensable water. By scrubbing out the CO_2, this disadvantage can be overcome to a certain extent. The H_2 usage with iron catalysts is small. Consequently, after the CO_2 has been scrubbed out of the end-gas, the remaining gas contains approximately 60 to 65 percent H_2 when water gas was used originally. When mixed gas was used to start with, a final end-gas containing 70 to 75 percent of H_2 is obtained after the CO_2 has been scrubbed out and when a starting gas os composition 20 percent CO

- 79

and 75 percent H_2 is employed, an end-gas results containing 90 percent H_2. For this reason, the end-gas has too small a density and does not correspond to the city gas requirements.

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

It is thinkable that a small addition of nickel respectively 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 one and five percent nickel respectively cobalt 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 $235^{\circ}C.$, in one case directly, and in another case, after a previous H_2 treatment had been given the catalyst. 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 is somewhat inferior to the nickel-free catalyst, whereas with a content of 5 percent cobalt, the activity does not seem to have been impaired as yet.

(Bahr)XIV. Reduction of the CO_2 on Iron Catalysts.

In the previous chapters, we have referred repeatedly to the fact that the end-gas obtained from carrier-free iron catalysts has a high content of CO_2. 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 seems astonishing. Especially is this true since CO_2 is reduced with noticeable speed already at $150^{\circ}C.$, when cobalt or nickel catalysts are present. The explanation may be that the iron catalyst in the presence of cobalt and nickel is not in a position to reduce CO_2 at low temperatures. As has been investigated by Kuester[5]

----

[5] Kuester, H., Brennstoff-Chemie 17, 203, (1936).

----

no noticeable reduction of CO_2 to methane occurs if the temperature is below $300^{\circ}C.$, and only at elevated temperatures in the range of $350=400^{\circ}C.$, will iron catalysts reduce CO_2 to methane. However, at temperatures of around $200^{\circ}C.$, a reduction of CO_2 to CO will occur.

The kieselguhr catalysts which are in a position to 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: A Fe-Cu-MnO (4:1:1) (kieselguhr)(1:1) catalyst was used, and the temperature in the be-

ginning was 150°C. It was permitted to act on 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 methane hydrocarbons. The latter had a carbon number equal to 1.9, hence, observation by Kuester was confirmed (see reference 5/), 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 an unessentially small amount, and eventually reached 21 percent. In addition to 10.4 percent residual CO_2, the reaction gas also contained 4.7 percent CO and 3.2 percent CH_4 hydrocarbons with a carbon number of 1.37. On the cold section of the reaction tube, a small amount of yellow oily products condensed out. A calculation showed that the CO_2 (on 100 percent basis) was converted in the following manner by the catalyst when working at 350-400°C.:

Temp., °C.	Percent		
	Unchanged CO_2	to CO	to CH_4-KW
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 because the sum total of the unconverted and converted CO_2 amounts to over 100 percent.

The result of the described experiments may be summarized by saying that even with the iron catalysts which are capable of forming some reaction water, a reduction of the CO_2 was not observed at the reaction temperatures of the benzene synthesis.

Thus may be explained the fact that in the reaction gases obtained from iron catalysts, appreciable quantities of H_2 can co-exist in these gases with large or next to large quantities of CO_2.

(Meyer)

XV. Copper-free Iron Catalysts.

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 "Geammelten Abhandlungen zur Kenntnis der Kohle", Vol. 10. Of special interest are the results obtained with iron-aluminum respectively iron-silicon alloy catalysts.6/ Contrary to the nickel respectively cobalt skeleton alloy catalysts,

6/ Brennstoff-Chemie 15, 107 (1934).

iron-aluminum and iron silicon alloys, after dissolving out 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 when working with iron alone (without copper) may be seen from the following investigations.

A. Preliminary Experiments.

In order to ascertain what the catalytic activity of a pure ferrous catalyst is (with respect to the CO hydrogenation), greatest care was taken that during the preparation of such a catalyst, oxidation to the ferric condition was avoided as much as possible.

In the beginning, we used $NaHCO_3$ as precipitant since the precipitations obtained with Na_2CO_3 or K_2CO_3 have a tendency to discolor very rapidly and change from green or black into brown. The precipitation with $NaHCO_3$, however, seems to be much more stable. The preparation of ferrous carbonate from $FeSO_4$ and $NaHCO_3$ was accomplished in the manner that the hot solution of $FeSO_4$ was added 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 presence of CO_2 and washed free of sulfates by using boiled hot water. The drying of the $FeCO_3$ was accomplished in a vacuum at room temperature. The catalytic activity of this catalyst was only very slight (2.5 percent contraction at $245°C.$), and an increase could not be obtained by a previous reduction with H_2 at $400°C.$ In order to exclude any possibility of reducing the activity of the catalyst by any residual sulfate sulfur, ferrous nitrate was used as starting material for the preparation of $FeCO_3$. For this purpose, iron shavings were dissolved in very dilute nitric acid of a specific gravity 1.035. The solution process was carried out in the cold, the precipitation of the ferrous nitrate was 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. The further processing of the ferrous formate solution occurred as already stated 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 $42 \, g./m^3$ 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 noticed. It is therefore apparent that the activity of the $FeCO_3$ catalyst, according to this method, is not reproducible. The precipitation of ferrous formate with $NaHCO_3$ in presence of kieselguhr lead to catalysts which were almost inactive. At the same time, 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 49.

Table 49

Activity of Ferrous Carbonate Prepared in Various Manners

Exp. No.	Mode of preparation	Carrier	Pretreatment	Exp. Temp., °C.	Maximum contraction, percent	Max. yields of liquid products g./ mixed gas
1	FeSO$_4$ + NaHCO$_3$	without	Mixed gas immediately	245	2.3	-
2	" "	"	H$_2$ 400°	245	2.0	-
3	Fe(NO$_3$)$_2$ and NaHCO$_3$	"	Mixed gas immediately	238	4.0	-
4	Ferrous formate and NaHCO$_3$	"	"	242	26.0	42
5	As 4, (re-test)	"	"	242	5.0	-
6	Ferrous formate and NaHCO$_3$	kieselguhr	"	245	3.0	-
7	FeSO$_4$ and Na$_2$CO$_3$	without	"	242	0.0	-
8	Ferrous formate and NNa$_2$CO$_3$	"	"	242	12.0	-

In Section II, 5Fe-1Cu catalysts were described in detail which were prepared by precipitating the chloride from a hot solution by using Na$_2$CO$_3$ precipitant. These catalysts were alkalized with 1/4 percent K$_2$CO$_3$, 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 50 contains the results which were obtained with an analogously prepared catalyst which was copper-free however, and contained various quantities of K$_2$CO$_3$.

Table 50.

Iron Alone, Prepared from FeCl$_2$ by Precipitation with Na$_2$CO$_3$.
Various Quantities of K$_2$CO$_3$ in the Catalyst

Exp. No.	Catalyst composition	K$_2$CO$_3$ contents, percent	Contraction in percent after days 7	14	21	Yield in 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	" "	1/8	14	17	20	33	" "
3	" "	1/4	18	17	23	30	" "
4	" "	1/2	13	18	20	25	"

The influence of the K$_2$CO$_3$ addition does make itself felt just as pronounced as in the case of the copper-containing catalysts. This, of course, only refers to the catalysts which were prepared from FeCl$_2$. With other modes of preparation as will be shown in a later chapter, a subsequent addition of K$_2$CO$_3$ can cause a considerable increase in activity. The catalysts precipitated from FeCl$_2$ and containing various quantities of K$_2$CO$_3$ require a long time of induction just as the K$_2$CO$_3$-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, whereas with the addition of 1/8 percent K_2CO_3, 33 grams, with the addition of 1/4 percent K_2CO_3, 30 grams, and with 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 degrees higher than for the corresponding copper-containing catalysts. After 3 weeks of operation, a further increase in activity was observed in no case.

(Ackermann)

B. Principle Experiment.

1. Dumped-weight-and-catalytic-activity.

   a. Mode of preparation and dumped weight.

In spite of the very voluminous and varied research which was done on catalysts, no information has been obtained so far from which one could predict just how good and how active a certain catalyst would be. In all cases, it was found 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 catalytic activity. It was pointed out that chemical changes might occur in the iron catalysts during the synthesis which would not have a connection to the dumped weight of the catalyst to start with, and also, it was pointed out 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.

Procipitations:

The acqueous solutions of ferrous chloride and ferric nitrate are precipitated with acqueous solutions of sodium carbonate, potassium carbonate, and sodium hydroxide and potassium hydroxide. The conditions, such as concentrations, temperature, and addition of reactants, varied in all cases. The precipitant was always dissolved in a quantity of water which was equal to a volume of 3/4 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 made 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 51 and 52, the dumped weights vary between 0.26 percent and 1.00 percent. There seems to be a fundamental difference in the dumped weights of the precipitated 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 oxi-hydrate 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 a dense crystalline precipitate which is easily filterable. The decomposition sets in already as soon as the washing operation is begun, and as soon as the air has access to it. It is first gray and then finally changes over to black. (After a longer period of contact with the air, the black mass changes into a reddish-brown ferric hydroxide.) When dried at $110^{\circ}C$., the main quantity of the CO_2 is driven off the ferrous carbonate and causes a very pronounced loosening of the mass. This loosening is the more pronounced the denser (larger crystals) the original ferrous carbonate was. Those precipitates which were most easily filterable showed that they 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 51, precipitation 5:10).

Table 51.
Dumped Weight with Normal Precipitation of
Ferrous Sulfate, Ferrous Chloride, and Ferric Nitrate with Soda

Iron salt	Exp. No.	Concentration in grams of iron per liter of solution	Temp., °C.	Dumped weight
Ferrous sulfate	1	50	20	0.35
	2	50	100	0.43
	3	10	20	0.50
	4	10	100	0.42
Ferrous chloride	5	100	20	0.50
	6	100	100	0.56
	7	50	20	0.43
	8	50	100	0.31
	9	10	20	0.58
	10	10	100	0.51
Ferric nitrate	11	50	20	1.00
	12	50	100	0.83
	13	10	20	0.83
	14	10	100	0.87

Increase of the temperature ($100^{\circ}C$.) as well as increase in concentration caused a noticeable reduction in the dumped weight. With reversed precipitation (Table 52), however, small dumped weights were only then obtained when chloride ions were added to the soda solution in advance in the form of NaCl (Table 52, Experiments 21 and 22). The observation may be explained by assuming that in the presence of chloride ions, the seeding of the crystals proceeds slowly. At the

[*] Normal precipitation - addition of precipitant to Fe-salt solution.
Reverse precipitation - addition of Fe-salt solution to precipitant.

same time, the velocity of crystal growth of the FeCO₃ 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 soda solution before the precipitation is carried out.

Table 52.

The Dumped Weight with Reverse Precipitation of Ferrous Sulfate, Ferrous Chloride, and Ferric Nitrate with Soda

Iron salt	Exp. No.	Concentration in grams of iron per liter of solution	Temp., °C.	Dumped weight	Remarks
Ferrous sulfate	15	50	20	0.39	
	16	50	100	0.39	
	17	10	20	0.48	
	18	10	100	0.48	
Ferrous chloride	19	50	20	0.37	
	20	50	100	0.43	10 grams of
	21	50	100	0.32 ←	NaCl to 10
	22	50	100	0.28	grams of iron
	23	10	20	0.50	
	24	10	100	0.59	20 grams of
					NaCl to 10
Ferric nitrate	25	50	20	0.83	grams of iron
	26	50	100	0.87	
	27	10	20	0.74	

Precipitations with Potash.

The same observations were made when the corresponding precipitations were carried out with K₂CO₃. Here we succeeded, for instance, with the reverse precipitation of 50 grams of iron per liter of ferrous chloride at 100°C., to reduce the dumped weight from 0.46 to 0.25 by the addition of KCl to the K₂CO₃ solution. The dumped weights of the precipitations of the three iron salts with potash, in general, were in good agreement with those obtained by precipitating with soda solutions. Consequently it is not necessary to recite these values.

Precipitations with Sodium Hydroxide.

The precipitations with sodium hydroxide give, in all cases, high dumped weights. The results of these precipitations do not depend whether ferrous or ferric salts are used. The dumped weights obtained vary 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. By drying, it does not loosen up. On account of the ease with which it can be

oxidized after the drying operation, it chiefly consists of ferric oxide. The dumped weights of all the catalysts which appear first as ferric oxide slates depend somewhat on the size of the powder: Powdered by means of a mortar:

10 minutes	15 minutes	20 minutes
0.71	0.61	0.59

b. **Catalytic Investigations of Catalysts With Various Dumped Weights.**

We use 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 53 contains the various catalysts arranged according to their increasing dumped weight. Considering catalysts which 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: High activity decreases for large dumped weights. Small activity decreases with small dumped weights.

Table 53.

Dumped Weights and Catalytic Activity of Soda
Precipitated Ferrous Chloride and Ferric Nitrate
Catalysts (non-alkalized)

Iron salt	Catalyst number	Dumped weight	Max. contraction, percent	Temp., °C.	After hours of operation
Ferrous chloride	1	0.26	8	250	120
	2	0.30	4.5	250	46
	3	0.42	8.5	240	64
	4	0.43	14	250	46
Ferric nitrate	5	0.83	22	240	90
	6	0.83	21	240	90
	7	0.87	23	240	90
	8	1.00	26	250	71

This finding is in contradiction with 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 better suited means of testing the catalytic properties should be perhaps the determination of the heat of adsorption which may be readily obtained as the heat of wetting when ethanol is used for instance. Thus, in accordance with the catalytic results, we found that a catalyst precipitated with soda from ferrous chloride and having a dumped weight of 0.31 exhibits a heat of wetting of only 2.3 calories per one gram of iron, when 96 percent of alcohol was used. The corresponding precipitated ferric nitrate catalyst with the dumped weight of 0.83 had a heat of wetting of 9.4 calories per one gram of iron. Summarily, it can be said that dumped weight determinations are not suited to predict the catalytic properties of iron catalysts. This goes for ferrous as well as ferric salts. 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 53 must have contained still considerable amounts of Na_2CO_3. This was probably responsible for the higher activity which these catalysts exhibited when compared to the chloride catalysts.

Table 54.

Dumped Weights and Catalytic Activity of Soda Precipitated
Ferric Nitrate Catalysts Exhaustively Washed in Comparison
to NH_3 Respectively $(NH_4)_2CO_3$ Precipitated Ferric Nitrate Catalysts (non-alkalized)

Iron salt	Cat. No.	Precipitant	Dumped weight	Temp., °C.	Max. contraction, percent	Hours of operation
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	"	1.00	234	11	120
	5	"	1.00	234	11.5	120

As Table 54 shows, the activity of thoroughly washed soda precipitated catalysts is not higher than the activity of the precipitated ammonia or ammonium-carbonate precipitated catalysts.

2. Determination of the Necessary Alkali Quantity Needed for Alkalization.

a. Estimation of alkali quantity according to chlorine contents in catalyst.

The addition of alkali carbonate acts similarly activating upon the iron one-component catalysts than it does upon the multi-component catalysts. In order to study the effect of the alkali, an experiment was carried through for 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 even be unfavorable. As the experiment reveals, however, (Table 55), this assumption does not seem to hold because the activity kept on increasing with increasing alkali addition, and it increased independent of the quantity of chloride present which was supposed to interact with the alkali.

Table 55.

Influence of Alkalization of a Catalyst Prepared from Ferrous Chloride with Soda
at 100°C., containing an Equivalent Amount of Alkali, twice the Equivalent Amount
and Ten Times the Equivalent Amount of Alkali

Chloride contents: 0.026 percent, requires 0.051% K_2CO_3 for neutralization

K_2CO_3 percent	Temp., °C.	Contraction, percent	Hours of operation
0	240	6	160
0.05	240	10	160
0.10	240	15	160
0.50	240	17	160

b. Excess alkalisation and removal of not-adsorbed alkali quantities by suction respectively washing.

During the alkalisation of catalysts, we found, generally, that the alkalinity of the slurry formed with the K_2CO_3 solution decreased after a short time. This we believe to be due to the fact that alkali is adsorbed on the catalyst. In the following experiment, therefore, we more or less left it up to the catalyst to take up according to its own choice, an optimum alkali quantity. A catalyst precipitated from ferric nitrate with soda was impregnated with 1/2 percent K_2CO_3 when still moist. From samples (c) and (d), the alkalization liquor was removed by suction and sample (d) was washed twice. Table 56 brings out that with increasing subsequent removal of the K_2CO_3, the activity decreased.

Table 56
Ferric Nitrate - Precipitated Catalyst, Alkalisation and Subsequent Removal of Alkali by Suction and Washing

Sample	Pretreatment percent K_2CO_3	Temp., °C.	Activity: Percent Contraction After Days of Operation				
			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% removed by suction	232	11.5	15	15.5	21	--
d	1/2% removed by suction and washing	232	11	10	8.6	11	

Aside from the finding that the possible adsorption of the optimum alkali quantity which might have taken place on the catalyst was not very 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 which was three times as large as the quantity of K_2CO_3 added for the purpose of 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 pre-alkalised by the precipitating soda. From this may be explained, without any difficulty the slowly increasing activity of sample (a), the course of the activity increase is characteristic for soda alkalization. Likewise the rapid decrease in activity of sample (b) may be due to over alkalization (present Na_2CO_3 and 1/2 percent K_2CO_3)

c. 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, however, containing 1/2 percent K_2CO_3. For a non-alkalized ferric nitrate catalyst the contraction was 2.7 percent and for the ferric nitrate catalyst alkalized with 1/2 percent K_2CO_3, it was 23.5 percent. As one can see, the activity of the non-alkalized catalysts which are obviously free of alkali is very small. The activation with alkali is especially pronounced in the case of the ferric nitrate catalyst.

d. Exhaustively washing the ferric nitrate catalysts precipitated with soda.

According to experiences made 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 alkali quantity which was necessary for such a catalyst. In order to be independent during the determination of the optimum alkali quantity, some alkali contents of some residual alkali quantities still present in the catalyst (due to more or less thorough washing of the catalyst), the washing operation of the catalysts was followed up by alkali determinations of the wash water (titration with HCl) so long until no worthwhile quantities of soda were removed any longer from the catalyst.

In this manner, the so far most active iron one-component catalyst was obtained which when alkalized with 1/2 percent K_2CO_3 gave a contraction up to 31 percent and yielded 55 grams of liquid hydrocarbons (oil + benzine) 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.

3. Most Effective Iron One-Component Catalyst.

a. 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 the 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 one liter of water for each washing. Then it was dried in air at 110°C. for 20 hours, and the dried and brittle catalyst was powdered in a mortar.

b. Alkali quantity and catalytic activity.

Alkalization:

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

From Table 57, it may be seen that with increasing alkali quantities, the activity increases. The catalyst containing 1/4 percent K_2CO_3 furnished its maximum contraction already 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, already after 3 days. The time of in-

[*] The ferric nitrate which was used for this and further experiments was prepared by dissolving technical iron in dilute nitric acid and following oxidation of the ferrous nitrate solution with concentrated nitric acid in the heat.

duction which in every instance was no longer for this catalyst than for an iron copper catalyst goes through a maximum with a K_2CO_3 content of 1/8 percent. As will be shown by time-tests, catalysts which require a long time for induction are less susceptible to fatigue than catalysts which require a short time for induction. After 14 days of operation, the catalyst with 1/4 percent K_2CO_3 formed already yellow products. At the same time, the yield of liquid hydrocarbons had decreased already by 8 g./m³. The non-alkalised catalyst gave a contraction of only 10 percent for the whole time of operation.

c. Catalytic activity during time-tests.

The experimental results in Table 58 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 - 40 grams up to the 22nd; and 40-30 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 3rd 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, consequently causes just as good an average yield for 38 days of operation than the addition of 1/8 percent K_2CO_3. Possibly the optimum alkali quantity is somewhere between 1/8 and 1/4 percent.

Table 57.
Activity Determination of a Precipitated Ferric Nitrate Catalyst
(Precipitated with Soda) which was Exhaustively Washed.
Influence of the Quantity of K_2CO_3, Operating Temperature, 233-235°C.

Days of oper- ation	0 percent K_2CO_3 Con- traction, percent	Liquid products g./m³	1/16 percent K_2CO_3 Con- traction, percent	Liquid products g./m³	1/8 percent K_2CO_3 Con- traction, percent	Liquid products g./m³	1/4 percent K_2CO_3 Con- traction, percent	Liquid products g./m³
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

Table 58

The Behavior of Soda Precipitated Ferric Nitrate Catalysts
which were Exhaustively Washed and which were in Operation for a longer Period of Time

Operating Temperature: 233-235°C.

Days of operation	Catalyst No. 1		Catalyst No. 2		Catalyst No. 3[*]	
	Con-traction, percent	Liquid products g./m³.	Con-traction, percent	Liquid products g./m³.	Con-traction, percent	Liquid products g./m³
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	---	36.5	---	---
31	---	---	---	---	27	37.2
38	26.3	39.9	21.5	28.3	26.0	33.6

[*]Catalyst No. 3 was prepared in the same manner as Catalyst No. 2 (fresh pre-cipitation). The above figures show that it was even somewhat superior to Catalyst No. 2.

d. Pelleting and Catalytic Activity.

The catalyst which was impregnated with 1/4 percent K_2CO_3 was extruded through the pelleting machine (cross-section-- mm. thickness, 1 to 2 mm). The increase of activity was somewhat more rapid than in the case of non-pelleted catalysts. The activity decrease, however, was that much faster. The maximum contraction was reached already after 3 days, and the yield was then 54 grams of liquid hydrocarbons. On the 10th day of operation, it had decreased to 50 grams, be-tween the 10th and 14th days, it varied between 50 and 40 grams, and at the end of the 22nd 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.

e. Conversion of CO with Water-vapor at Synthesis Temperature.

In connection with the benzine synthesis, we were also interested in finding out whether the iron one-component catalyst is already in a position to ac-celerate the water-gas equilibrium at benzine synthesis temperatures.

A catalyst which contained 1/4 percent K_2CO_3 and was prepared by precipitating ferric nitrate was allowed to act on mixed gas at 235°C, for 46 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 lead 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 contents had decreased by 36.6 percent. According to this, the expansion was only 5 percent. (According to the water-gas generation and assuming a CO_2 formation, an expansion of 32 percent is expected.) Consequently, we are justified to conclude that parallel to the water-gas reaction, the benzine synthesis occurs simultaneously. If one assumes that one CO_2 is formed from approximately $2CO + H_2$ at conditions of the benzine synthesis, one is in a position to calculate approximately the original water-gas conversion. According to this, around 20 percent of the CO was converted with water. After 24 hours, the CO_2 decreased to 20 percent, whereas the expansion increased simultaneously up to 9 percent. We conclude from this that the benzine synthesis had decreased more rapidly than had the water-gas reaction. At the same time, we found that one 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 is in a position to shift the water-gas equilibrium towards the CO_2 direction. This discovery, however, is not yet sufficient reason and does not give sufficient basis for explaining why the benzene synthesis takes a different course over the iron one-component catalyst than it does over cobalt and nickel catalysts.

4. Regeneration Experiments.

a. With H_2 at Synthesis Temperature.

A catalyst which, after 20 days of operation, gave only the small contraction of 27.5 percent and which furnished yellow oil already, 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 switching back to mixed gas, yellow products formed just as before. The contraction, after the H_2 treatment was practically the same as it was before; however, after 4 days of operation, it decreased to 21 percent. Consequently, no regeneration had occurred.

b. With Super-heated 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 already after 3 days of operation. In all cases we observed that the liquid products remained yellow. Consequently, no regeneration had taken place.

- 93 -

c. 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 brought out, therefore, that so far we have not succeeded in regenerating an iron one-component catalyst.

5. 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 are longer. After approximately 8 days of operation with 1/4 and 1/2 percent Na_2CO_3, maximum contractions of 23, respectively 28 percent 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 remarkable 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, gave still 36 grams of liquid hydrocarbons. For both catalysts, however, the oil was yellowish in color. 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. We are talking about a ferric nitrate catalyst precipitated with soda which was, however, not washed exhaustively. (See Table 56, 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 only after 20 days of operation (27 to 28 percent, maximum yield, 46 grams); and between the 8th and 42nd 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.

6. Multi-component Catalysts which were Precipitated in the Same Manner as the Best Iron One-component Catalysts.

a. Iron-Copper Catalysts.

Stimulated by the good results with iron one-component catalysts, it was suggested to 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 a deterioration resulted. We precipitated ferric nitrate-cupric nitrate solutions in the same manner with soda as we precipitated the iron salts from which the pure iron catalyst was made. The copper quantities used were one percent copper, 5 percent copper, and 20 percent copper. For the first series of experiments, catalysts were used which 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 a further series of experiments, the catalysts were alkalized with 1/4 percent K_2CO_3. The contraction went up to 27 to 28 percent independent of the copper quantity. The yield of liquid hydrocarbons was, in the best case, 49 g./m³. After 24 days of operation, the products formed were yellow already at an average contraction of 26 percent and 38 grams of yield.

   b. 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 one part of zinc, and 10 parts of iron to one part of zinc acted practically 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 had a longer time 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.

7. Ferric Nitrate Decomposition Catalysts.

If we would have succeeded in preparing decomposition catalysts which had the same activity as the precipitated catalysts, we could have cheapened the catalyst considerably by saving the soda, the wash-water, and some time of operation.

As starting material, we used the ferric nitrate solution, which we have resorted to before, when preparing the precipitated catalysts. 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 small pieces, such as were obtained after the decomposition. As compared to the precipitated catalysts, a faster decrease of activity is noticeably because after 13 days of operation, the contraction had decreased to 25 percent and the yield to 38g./m³.

A treatment with mixed gas followed by air, and vice versa, prior to taking the catalyst into operation, proved to be more unfavorable than a treatment with mixed gas alone.

We added some starch to the catalyst to be pelleted (one 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.

XVI. Investigation of the Reaction Products on the Iron Catalyst.

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 semi-plant scale operation.

(Bahr) Contents of Unsaturated Hydrocarbons in the Synthesis Products (Benzene + Oil) as Obtained on Iron Catalysts.

We found that an iron-copper-manganese (4:1:1) catalyst containing one 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
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 contents of unsaturated compounds in the reaction products varies between 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 benzene 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 takes up a certain quantity of paraffin which it retains within its body just as we have found it to be the case with cobalt catalysts. We extracted this paraffin out of the catalyst

using benzol or hydrogenated Kogasin I. Thus, we obtained up to 30 percent of paraffin, based on the catalyst weight, by extracting. The paraffin quantities 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 lifetime, did not have enough time to be more completely saturated with paraffin.

A more close 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 extracting it with a solvent such as ether. By multi-extractions, with ether, of the high-melting portion, again a product could be obtained which 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.

(Meyer)

Table 59
Paraffin Quantities Retained by the 5Fe-1Cu Catalyst, Relationship
Between this Paraffin Quantity and K_2CO_3 Contents of Catalyst (10 grams Fe)

Exp. no.	K_2CO_3 contents, percent	Days of operation	Consumption of mixed gas per m^3	Extraction of paraffin in grams	Paraffin in $g./m^3$ of mixed gas	Contraction per- cent	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	0.7	8.2	11.7	7	4

Table 59 gives information about the paraffin quantities contained in iron cata-lysts with varying amounts of K_2CO_3. This data is for a definite period of operation. The third last column indicates the quantity of paraffin which was obtained from the catalyst by extracting it with synthetic benzene (fraction 80-100°C.). The quantity of paraffin given there is given as grams per cubic meter of mixed gas put through the unit. The catalyst with 1/4 percent K_2CO_3 contained approximately twice as much paraffin as did the catalyst which con-tained no K_2CO_3. A catalyst containing 1/2 percent K_2CO_3 after being in opera-tion for 20 days, had already taken 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 are contained in the catalysts alkalized with one percent, respectively 2 percent, K_2CO_3. The decrease of activity of the cata-lysts increases with increasing paraffin formation (last column). To this should be added, that the decrease of the activity does not depend on the quantity of the paraffin taken up by the catalyst, but rather depends on the simultaneous appearance of decomposition products of the paraffin. These da-

composition products show up in a more pronounced way in the case where heavily alkalized catalysts are used. For the catalysts containing little K_2CO_3, the appearance of the decomposition products does not set in as early.

Summarily one can say that when iron catalysts up to approximately 12 grams of high-melting paraffins may be extracted from the catalyst per cubic meter of mixed gas put through, provided that the catalyst contains 1 to 2 percent K_2CO_3. In the interest of good lifetimes of the iron catalyst, it is recommended, therefore, that only small to moderate alkali quantities should be added.

(Bahr) Acid Products.

Just as in the case of cobalt catalysts, so also with iron, not only benzene, oil, and paraffins are obtained, but small quantities of acid products as well. When the synthesis is carried out with carrier-free catalysts, these acid products are chiefly found in the oil; but also to some extent in the paraffin, which can be extracted from the catalyst. Such acid products may be obtained from the catalysts almost immediately if the catalyst is boiled with a one to 2 percent normal Na_2CO_3 or NaOH solution. One then obtains quickly colored yellow extracts which after an acidifying extraction with ether and evaporating off the ether, leave behind semi-liquid products of pungent odor which reminds one of the higher fatty-acid series. In one case we obtained 0.5 grams of such acid products after extracting 40.5 grams of a catalyst having served for some time, that is, approximately one percent of the catalyst weight. Perhaps the activating alkali contents of the catalyst gradually enters into reaction with the acid products and forms soaps. It is possible also that to a lesser degree fatty-acid salts of iron, copper, and manganese might appear. In this connection, an older experiment is of interest during which the used-up catalyst, after the 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 have still been present in the catalyst, it was boiled out with ether, and thereafter it was refluxed with dilute sulfuric acid. When the acid was added, almost violent CO_2 evolution occurred. After filtering off the insolubles, the sulfuric acid solution was extracted with ether in the perforator, and the insoluble residue from the catalyst was boiled out with ether as well. Both extractions were combined, and after evaporating off the ether, 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 was obtained and 4.4 percent "acid products".

It does not appear that the decrease in catalyst activity should be caused by a combination of the acid materials with the alkali of the catalyst (to form fatty-acid salts). In Section III, as already mentioned, we added one percent of potassium acetate to the catalyst without impairing the activity of the catalyst.

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

Strangely enough, the reaction water, and the liquid products obtained from the water-forming kieselguhr catalyst react essentially 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 perhaps they are formed just as abundantly, but are retained to a greater degree by the carrier catalyst.

XVII. Advantages and Disadvantages of Iron Catalysts.

Summarily the following may be said about the advantages and disadvantages for using iron catalysts:

1. When iron catalysts are used, we do 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. An addition of expensive thorium is not required. The preparation of the iron catalysts can be carried out technically in the same type of apparatus as the cobalt catalyst is prepared, that is, either by dissolving iron in nitric acid or hydrochloric acid. For the precipitation in both cases, soda may be used.

2. The iron catalyst may be taken into operation with mixed gas immediately at the proper reaction temperature without a 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 lifetime 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 previous extraction). By doing so, it regains its old activity. This is quite contrary to cobalt catalysts.

5. The highest yield so 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 (benzene, oil, and paraffin) are qualitatively the same as in the case of the cobalt catalysts. The iron catalyst offers the possibility to produce benzenes with a high content of unsaturates.

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