

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 Erdoel-synthese"^{1/}. In the following, a short

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 $1Al(OH)_3 - 1/3NaOH$. 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 however. 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 calculated 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 catalysts 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 dissolving iron shavings in various acids; in some other cases, the ferrous compounds were bought as such, for example, iron-II-sulfate and iron-II-chloride.

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

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

Iron shavings were dissolved in dilute formic acid, and the resulting iron-formate solution was precipitated in the cold with sodium bicarbonate and in the presence of copper nitrate (20 percent of copper). The washing of the catalyst was carried out in a CO₂ atmosphere in order to avoid an oxidation of ferrous carbonate to ferric hydroxide. The drying of the catalyst was carried 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 H₂, 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 corresponding to the production conditions, we investigated how an alkalization of the manganese would effect the activity. We found that alkalization of the manganese did not improve the efficiency of the catalyst. For the sake of clearness, 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 Formate by Precipitation with Sodium Bicarbonate)

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

8- 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 FeSO_4 respectively FeCl_2 by Precipitation with Na_2CO_3

Exp. No.	Catalyst Composition	Preparation Conditions	Exp. Temp., °C.	Maximum Contraction Percent	Days	Max. yields in l./cm of mixed gas
1	5Fe - 1Cu	FeSO_4 and $\text{Cu}(\text{NO}_3)_2$ precipitated in the cold with Na_2CO_3	242	14	6	14
2	" "	" " " " " "	250	23	5	25
3	5Fe-1Cu-1Mn	FeSO_4 -Cu-Mn-nitrate precipitated in the cold with Na_2CO_3 .	240	14	4	22
4	" " "	FeCl_2 , Cu-Mn-nitrate precipitated in the cold with Na_2CO_3 .	240	22	3	32
5	" " "	" " " " " "	235	20	4	30
6	" " "	FeCl_2 , Cu-Mn-nitrate precipitated in the cold with Na_2CO_3 , catalyst extracted for 24 hours with water.	235	12	4	18

Experiments 1 and 2, in Table 2, show that the efficiency of the catalyst produced from iron-sulfate is lower than that of the catalysts produced from ferrous formate. The yield amounted only to 14 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 FeCl_2 was used instead of FeSO_4 , this yield increased to 32 grams (Experiment 4). When the experiment was repeated, 30 grams were obtained at a temperature of 235°C. (Experiment 5).

We believed, at first, that the poor catalytic activity of the catalysts produced from FeSO_4 and FeCl_2 could be explained by attributing it to unfavorable influences caused by the presence of some Na_2SO_4 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.

C. X. 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 . (Experimental) 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 nitrate 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 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 5.
Influence of the Addition of Potassium Carbonate

Exp. No.	Catalyst composition	Mode of preparation	K ₂ CO ₃ contents referred to iron	Exp. Temp., °C.	Max. contraction, percent	Max. yields in g./m ³ of mixed gas
1	5Fe-1Cu-1Mn	FeSO ₄ , Cu- and Mn-nitrate precipitated in the cold with Na ₂ CO ₃	without	240	14	22
2	" " "	" " "	1/2%	230	29	43
3	" " "	FeCl ₂ , Cu- and Mn-nitrate precipitated in the cold with Na ₂ CO ₃	without	240	22	32
4	" " "	" " "	1/2%	230	30	48
5	" " "	FeCl ₂ , Cu- and Mn-nitrate precipitated with NaHCO ₃	1/2%	232	28	45
6	" " "	Fe(NO ₃) ₃ , Cu- and Mn-nitrate precipitated with Na ₂ CO ₃	1/2%	232	25	35
7	" " "	Fe-Cu-Mn-nitrate thermally decomposed	1/2%	232	17	24
8	" " "	FeCl ₂ , Cu- and Mn-nitrate precipitated hot with Na ₂ CO ₃	1/2%	230	32	51
9	" " "	" " "	without	240	23	40
10	" " "	FeCl ₂ , CuCl ₂ and MnCl ₂ precipitated hot with Na ₂ CO ₃	1/2%	233	30	50
11	5Fe - 1Cu	FeCl ₂ , CuCl ₂ precipitated hot with Na ₂ CO ₃	1/2%	235	30	50
12	" " "	" " "	without	235	22	35
13	5Fe-1Cu-1/21g	FeCl ₂ , CuCl ₂ , MgCl ₂ precipitated with Na ₂ CO ₃	1/2%	235	23	37
14	5Fe-1Cu-1Mg	" " "	1/2%	235	21	33

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The optimum K₂CO₃ 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 K₂CO₃ 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 K₂CO₃, 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 K_2CO_3 Quantity Upon the Activity of the 5Fe-1Cu Catalysts

Exp. No.	K_2CO_3 contents, percent	Exp. Temp., °C.	Max. contraction percent	Max yields in g./m ³ 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	13	21
					7	32
6	1	228	29	28	5	9
7	2	228	22	-	7	4

Besides causing a better yield, the addition of small quantities of K_2CO_3 exerts a favorable influence upon the 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 K_2CO_3 contents still give a contraction of 28 respectively 26 percent after 40 days of operation, whereas a comparative catalyst with 1/2 percent K_2CO_3 only furnishes 18 percent contraction after 21 days of operation, and 7 percent contraction after 32 days. With the addition of one percent K_2CO_3 , 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 K_2CO_3 was such that within 4 days the contraction decreased from 22 to 7 percent. The lifetime of a catalyst which was not subsequently alkalinized (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 K_2CO_3 Quantity Upon the Lifetime of the Catalyst
(5Fe-1Cu Catalyst)

Exp. No.	K_2CO_3 Contents	Yields, g./m ³ 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 K_2CO_3 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 K_2CO_3 , still 47 grams of liquid products per cubic meter of mixed gas were obtained, with a catalyst containing 1/8 percent K_2CO_3 , 45 grams, and with another catalyst containing 1/4 percent K_2CO_3 , still 37 grams of liquid products per cubic meter of mixed gas were formed. The average yield for six

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 K₂CO₃. We found that this catalyst (containing 1/2 percent K₂CO₃) 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 K₂CO₃ 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 K₂CO₃ additions showed that the maximum yields as well as the stability of the catalysts were reproducible.

Table 6.

Influence of K₂CO₃ Quantity and Length of Operation Upon the Ratio, $\frac{\text{Yield}}{\text{Contraction}}$

Exp. No.	K ₂ CO ₃ contents, percent	Days of operation	Con- traction percent	Yields in g./m ³	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 K₂CO₃ still exhibits a somewhat higher activity after 6 to 7 weeks of operation than the corresponding catalyst containing 1/8 percent K₂CO₃. 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 K₂CO₃ 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 K₂CO₃.

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 K₂CO₃-free catalyst. The lowest value, namely 1.8, refers to the catalyst containing the greatest amount of K₂CO₃. 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 K₂CO₃ 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.

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*Graphs referred to not available on microfilm.

X.D. 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 $105^\circ C$. 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., $^\circ C$.	Max. contraction	Max. yields in g./m ³ of mixed gas	Average yield g./m ³	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 impregnation 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.

S.E. 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 successfully. However, it is possible to produce small pellets by protruding the wet catalyst through small holes. These pellets exhibit excellent mechanical properties. Furthermore, we succeeded in getting a catalyst of good mechanical properties by adding 10 percent of starch^{3/} (referred to iron metal). The ac-

^{3/} Brennstoff Chemie, 14, 49, (1933).

tivity of these catalysts may be observed from Table 3. 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 ₂ CO ₃ content, percent	Conditions of preparation	Exp. Temp., °C.	Max. concentration, percent	Max. yields in g./m ³ of mixed gas		
					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.

4.F. Influence of the Addition of Na₂CO₃

After we had investigated the effect of K₂CO₃ 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 Na₂CO₃. From earlier experiments we know that Na₂CO₃ as well as K₂CO₃ 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 Na₂CO₃ is not quite as pronounced as the increase in activity of K₂CO₃ however.

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

The lifetime of the catalysts containing Na₂CO₃ was longer than that of the catalyst containing K₂CO₃.

Table 9.
Influence of Subsequent Addition of Na_2CO_3

Exp. No.	Catalyst composition	Na_2CO_3 content, percent	Yield in g./l 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 promoter especially since it is possible to regenerate the K_2CO_3 containing catalysts with greater assurance and safety. We shall report on that later.

The catalyst containing 1/2 percent Na_2CO_3 exhibits a somewhat higher activity than the corresponding K_2CO_3 catalyst and especially a better stability (Experiment 2). On the whole, however, it differs little from that containing 1/4 percent of Na_2CO_3 . At 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.

7.6. 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./l 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 1/3 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 led us to investigate whether such an addition to iron catalysts would result in an improvement similar to that of cobalt catalysts. The most prominent metal investigated as a third component was manganese.

It should be 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 these 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 dissipated. 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 precipitated catalyst which had corresponding apparent densities varying between 0.92 to 1.17.

With 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 240°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 CO₂ and H₂ (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 with a contraction of 25 percent, had the following composition:

	CO ₂	SKW	O ₂	CO	H ₂	CH ₄ -KW	^{Number} C- unit	N ₂
percent	18.4	1.4	0.3	8.3	59.1	3.7	1.51	2.8

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-K₂O 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 NH₃).

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, it was necessary nevertheless to add some additional alkali in order to obtain an active catalyst. The alkali (a dilute K₂CO₃ solution) was added to the still moist but already washed catalyst. Then the catalyst was dried at 10°C. and used for the reaction. When NaOH was used as a precipitant, the most favorable quantity of K₂CO₃ was between 0.5 and one percent K₂CO₃ 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 alkalinized 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 K₂CO₃, and in another, contained 2.5 percent K₂CO₃. 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 K₂CO₃ and 17.1 grams of paraffin from the catalyst containing 2.5 percent K₂CO₃. 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 K₂CO₃. (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 alkalinized 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 K₂CO₃, this total quantity amounted to 49.9 grams, and for the catalyst containing 2 percent K₂CO₃, the total yield was 51.5 g./m³ (apparently should be 2.5 percent K₂CO₃).

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 of copper, and 2.5 grams of MnO (plus 1 percent K₂CO₃) 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, CO₂ was formed and normally little water formation was observed. Detailed data on the relationship between yield, CO₂, 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 K₂CO₃ 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 K₂CO₃. 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 alkalinized 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.

NH₃. NH₃ 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 , $(\text{NH}_4)_2\text{CO}_3$)

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-KNO 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-KNO catalyst containing 0.1 percent K_2CO_3 is described (Fe:Cu:KNO = 10:2.5:2.5).*

Table 11.

Conversion (Mixed Gas) with Fe-Cu-KNO-0.1 percent K_2CO_3 (with Soda Precipitated) 10:2.5:2.5

Temperature, $^\circ\text{C}$.	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	31.2	76.4
percent going to H_2O (diff.)	8.3	11.9
$\text{H}_2\text{O}:\text{CO}_2$	1 : 9.8	1 : 6.4
Liquid products, g./m ³	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 31 percent of the CO-oxygen went to CO_2 and only 3 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-KNO quantity.

hours of operation.

	CO ₂	sKW	O ₂	CO	H ₂	CH ₄ KW	<i>Number</i> 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 K₂CO₃ was already sufficient. When a larger quantity of K₂CO₃ 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.

K₂CO₃. 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 K₂CO₃ 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 K₂CO₃ to the catalyst precipitated with K₂CO₃ probably would not cause the activity to increase any further, we investigated the influence which Na₂CO₃, Rb₂CO₃, and potassium acetate (each one percent) has as a promoter. We observed that the weaker base (Na₂CO₃) remained without influence, also potassium acetate had no influence. However, no damaging effects resulted from their addition. The addition of Rb₂CO₃ caused the appearance of the yellow-colored reaction products to occur earlier. The contraction was not increased by the addition of Rb.

(NH₄)₂CO₃. 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 CO₂ 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 K₂CO₃, and similar to the Na₂CO₃ 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 23°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 K₂CO₃. 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
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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.