

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. Fe-Cu-Cr₂O₃ + 0.5% K_2CO_3 .
8:2:2
2. Fe-Cu-Cr₂O₃ + 0.5% K_2CO_3 .
8:2:8

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 reduce any forming chromate, although the reduction temperature was 400°C. The corresponding decomposition products, having compositions 1 and 2, were even less active than the given precipitated catalysts.

Aluminum. By precipitation with soda from the nitrates, a Fe-Cu-Al₂O₃ 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-SnO₂ = 4:1:1 containing 0.5 percent K_2CO_3 also.

C. Appendix. - *Catalysts of special composition.*

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 232 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 alkalinized catalyst. Further details on the copper-free iron catalyst are discussed in Section (V).

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.

Iron (2)-carbonate. 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 24°C. The maximum contraction of 19 percent was observed at 25°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 (α Fe₂O₃ · 1H₂O) 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 Fe₂O₃. 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-H₂ reaction.

A. Preparation of the Synthetic Needle Iron Ore (α Fe₂O₃ · 1H₂O)

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(NO₃)₃ · 9H₂O) 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 H₂ 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 K₂CO₃ 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 m³., 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 H₂ 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 α -Fe₂O₃·1H₂O component as amorphous Fe₂O₃ instead of crystalline Fe₂O₃. 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 crystalline 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 4, 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 % of mixed gas. A specific influence of the thorium respectively manganese upon the activity of the catalyst could therefore not be observed. Regarding the life-time of the catalyst, it may be said that the thorium-containing catalysts are somewhat better than the manganese catalysts.

B-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 led 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-ores 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./m³ of mixed gas was obtained.

By heating commercial Fe₂O₃ under pressure (in presence of KOH at 160°C.) apparently unchanged Fe₂O₃ 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 Fe₂O₃. The maximum yield obtained with needle-iron-ore catalysts amounted to 53 g./m³ 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. conversion 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	" " "	15 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./m ³ 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 CuCO ₃ . No application of heat and pressure.	230	13	24	12	--	--
	Fe precipitate with ammonia after application of heat and pressure in presence of KOH mixed with CuCO ₃ .	230	30	49	47	41	--
3	Catalyst identical with Nos 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, m ³ of mixed gas	Remarks
2	" "	Cu plus thorium precipitated simultaneously with K ₂ CO ₃ 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.

V. Influence of Pretreatment of Iron Catalysts

(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 $105^\circ C$. The maximum activity is reached after a certain time of induction elapses which for the alkalis 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-In 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.

1. Influence of CO induction at synthesis temperature.

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 $235^\circ C$. 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 Pretreatment with CO

Exp. No.	Catalyst composition	Pretreatment of the catalyst	Exp. Temp. °C.	Percent			Average yield after 17 days of operation, g./m ³ of mixed gas
				contraction after 5 hrs.	Max. contraction, percent	Max. yield in g./m ³ mixed gas	
1	5Fe-1Cu-1Mn + 1/2% K ₂ CO ₃	Mixed gas immediately	228	5	30	49	47
2	" "	2 1/2 hrs. CO then mixed gas.	228	17	32	50	47
3	" "	2 1/2 hrs. CO, 2 1/2 hrs. H ₂ then mixed gas.	226	18	30	49	45
4	" "	2 1/2 hrs. mixed gas, 2 1/2 hrs. H ₂ then mixed gas.	228	31	30	49	44
5	5Fe-1Cu + 1/2% K ₂ CO ₃	Mixed gas at once.	230	after 2 hrs. 4%	31	55	-
6	" "	2 hrs. mixed gas, 2 hrs. H ₂ , then mixed gas.	230	after 2 hrs. 8%	32	52	-
7	" "	2 hrs. CO, 2 hrs. H ₂ , then mixed gas.	230	after 2 hrs. 16%	31	53	-

2. Influence of CO pretreatment at higher than synthesis temperature.

(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 CO₂ (up to 90 percent). After 1/2 to 3/4 hours; this CO₂ 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.

8-
(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 13 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 unfavorably than the normally pretreated catalysts. Especially is this true for pretreatment at higher temperatures. This effect is understandable if one takes into consideration that the iron catalyst is comparatively sensitive already at temperatures of around 250°C.

C. Influence of H₂ Pretreatment.

As already mentioned, contrary to cobalt and nickel catalysts, the iron catalysts can be used for the synthesis without a previous H₂ 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 H₂ treatment performed either at the reaction temperature or at some other higher temperature.

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 .

2.
(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 iron 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 some cases, a reduction of the catalyst at high temperatures may be advantageous as the following observation shows: A simultaneously precipitated Fe-Al catalyst (15 percent Al_2O_3 referred to iron), proved to be 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. Influence of the Addition of Carriers and Influence of the Mode of Addition.

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 these catalysts. With iron catalysts, however, we found that the addition of carriers generally produces unfavorable results, except in those cases where the catalyst was mixed with alkali carriers, such as for instance, Stuttgart Mass. In these instances, an activation is actually caused by the addition of the car-

ricers. 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.

Catalyst
A X. Fe-Cu-carrier ~~carriers~~ 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 $60g./m^3$ 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 $350^\circ C$. 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 $49 g./m^3$ 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 28 grams.

Table 16

Influence of the Addition of Carrier and Mode of Addition
Precipitation of Chloride with Na₂CO₃; 5Fe + 1Cu Catalyst

Exp. No.	K ₂ CO ₃ contents	Carrier, L. F. per 10 g. of Fe	Mode of Addition	Reduction Conditions	Max. contraction, percent	Behavior of the catalyst
1	1/4"	without	-	immediately, mixed gas	33 230°	58g., liquid products
2	1/4"	kieselguhr	mixed dry afterwards	"	32 232°	51g., liquid products, induction, 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 ₂ O 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 ₂ CO 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 ₂ CO ₃ contents	Carrier, % per 10 g. of Fe	Mode of addition	Reduction conditions	Max. contraction, percent	Behavior of the catalyst
14	1/4%	silica gel powder	added dry afterwards	immediately mixed gas	30 230°	56g. of liquid products. When silica gel is afterwards mixed in dry, the latter remains indifferent.
15	without	asbestos meal 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	1/4%	"	"	"	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 H₂ 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 H₂ 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 Al₂O₃ 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. Cr₂O₃ 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 Cr₂O₃ addition.

Table 17 (next page)

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_2CO_3

(5Fe-1Cu Catalyst)

Expt. No.	K_2CO_3 contents	Carrier, % per 10 % 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_2O_3	"	"	13 235°	Deterioration by Al_2O_3 no water formation.
6	1/4%	"	"	"	13 235°	
7	without	Commercial Cr_2O_3	"	"	22 230°	28 g. of liquid products
8	1/4%	"	"	"	29 230°	51g. liq. prod.)
9	without	"	added dry	"	15 230°	27g. " ")
10	1/4%	"	"	"	30 230°	54g. " ")

(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.

C. 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_2CO_3 , and the ratio of oxide powder and carrier was 1:1. As carriers, we used silica gel, kieselguhr, and ground Stuttgart Mass. With this mode of addition, no difference in activity was noticed for the various carriers.

Later 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 Stuttgart Mass (granulated and ground), silica gel, and kieselguhr. With this method of addition, no improvement over the carrier-free catalyst could be observed in any instance. The catalyst which contains Stuttgart Mass or silica gel 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 $250^\circ C$. with or without previous extraction of the paraffins.

2D. 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 $250^\circ C$. 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 $240^\circ C$. 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).

E. Fe-Cu-MnO-Kieselguhr Catalysts: Preparation of ^{some} ~~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.

1. 1(4 Fe-1Cu -1 MnO); 1 Kieselguhr 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 15 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 83 percent of the CO. The difference may be explained through the water formation of the kieselguhr catalysts.

A yield determination was not carried out for the 1:1 kieselguhr catalyst, since we found that the 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 unreplicable 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.