ginning was 150°C. It was permitted to act on a gas containing 14.8 percent CO_2 and 83.4 percent H_2. The temperature had to be raised to 200°C., before a small contraction of 3 percent could be measured. At 275°C., a contraction of 6 percent was observed, at 350°C. (4 liters of throughput per hour), 19 percent contraction was noticed. At this temperature, the reaction gas in addition to 10.7 percent residual CO_2, also contained 3.3 percent CO and 2.1 percent methane hydrocarbons. The latter had a carbon number equal to 1.9, hence, observation by Kuester was confirmed (see reference 5/), that the CO_2 is not only converted to methane in the presence of iron catalysts, but also to higher hydrocarbons. At 400°C., the contraction increased only an unessentially small amount, and eventually reached 21 percent. In addition to 10.4 percent residual CO_2, the reaction gas also contained 4.7 percent CO and 3.2 percent CH_4 hydrocarbons with a carbon number of 1.37. On the cold section of the reaction tube, a small amount of yellow oily products condensed out. A calculation showed that the CO_2 (on 100 percent basis) was converted in the following manner by the catalyst when working at 350-400°C.:

Temp., °C.	Percent		
	Unchanged CO_2	to CO	to CH_4-KW
350	58.8	18.2	21.8
400	35.4	25.0	23.0

At 400°C., a small analytical error was introduced into the determination because the sum total of the unconverted and converted CO_2 amounts to over 100 percent.

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

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

(Meyer)

XV. Copper-free Iron Catalysts.

Finally, we want to report on the results which we obtained with copper-free iron catalysts. With reference to earlier experiments, we want to refer to the "Geammelten Abhandlungen zur Kenntnis der Kohle", Vol. 10. Of special interest are the results obtained with iron-aluminum respectively iron-silicon alloy catalysts.[6] Contrary to the nickel ~~respectively~~ and cobalt skeleton alloy catalysts, iron-aluminum and iron silicon alloys, after dissolving out the aluminum with NaOH, were almost entirely inactive. An improvement did not result even when the catalysts were oxidized.

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[6] Brennstoff-Chemie 15, 107 (1934).

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

A. Preliminary Experiments.

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

In the beginning, we used $NaHCO_3$ as precipitant since the precipitations obtained with Na_2CO_3 or K_2CO_3 have a tendency to discolor very rapidly and change from green or black into brown. The precipitation with $NaHCO_3$, however, seems to be much more stable. The preparation of ferrous carbonate from $FeSO_4$ and $NaHCO_3$ was accomplished in the manner that the hot solution of $FeSO_4$ was added to a solution of $NaHCO_3$ under constant stirring. In order to assure complete precipitation, heating was continued for some time on the water bath under a CO_2 atmosphere. The grayish-white precipitate was then filtered in presence of CO_2 and washed free of sulfates by using boiled hot water. The drying of the $FeCO_3$ was accomplished in a vacuum at room temperature. The catalytic activity of this catalyst was only very slight (2.5 percent contraction at 245°C.), and an increase could not be obtained by a previous reduction with H_2 at 400°C. In order to exclude any possibility of reducing the activity of the catalyst by any residual sulfate sulfur, ferrous nitrate was used as starting material for the preparation of $FeCO_3$. For this purpose, iron shavings were dissolved in very dilute nitric acid of a specific gravity 1.035. The solution process was carried out in the cold, the precipitation of the ferrous nitrate was accomplished with $NaHCO_3$ in the manner already described. With this catalyst, a contraction of 4 percent was obtained during 8 days of operation.

As an alternative method for the preparation of $FeCO_3$, we resorted to the precipitation of ferrous formate by means of $NaHCO_3$. Ferrous formate was obtained by dissolving iron shavings in dilute formic acid. The further processing of the ferrous formate solution occurred as already stated above. With this $FeCO_3$ and an experiment temperature of 242°C., a maximum contraction of 26 percent was obtained. However, it should be mentioned that it took 10 days of operation to reach this contraction. The maximum yield of liquid hydrocarbons was 42 g./m^3 of mixed gas. When the experiment temperature was raised with another batch of $FeCO_3$, produced in the same way, a maximum contraction of only 5 percent could be noticed. It is therefore apparent that the activity of the $FeCO_3$ catalyst, according to this method, is not reproducible. The precipitation of ferrous formate with $NaHCO_3$ in presence of kieselguhr ~~lead~~ led to catalysts which were almost inactive. At the same time, a catalyst prepared by precipitating ferrous sulfate with soda exhibited no activity either. However, a $FeCO_3$ catalyst prepared from ferrous formate and Na_2CO_3 gave a maximum contraction of 12 percent. The results with the copper-free ferrous carbonate catalysts so far investigated are tabulated in Table 49.

Table 49

Activity of Ferrous Carbonate Prepared in Various Manners

Exp. No.	Mode of preparation	Carrier	Pretreatment	Exp. Temp., °C.	Maximum contraction, percent	Max. yields of liquid products g./m³ mixed gas
1	$FeSO_4 + NaHCO_3$	without	Mixed gas immediately	245	2.3	-
2	" "	"	H_2 400°	245	2.0	-
3	$Fe(NO_3)_2$ and $NaHCO_3$	"	Mixed gas immediately	238	4.0	-
4	Ferrous formate and $NaHCO_3$	"	"	242	26.0	42
5	As 4, (re-test)	"	"	242	5.0	-
6	Ferrous formate and $NaHCO_3$	kieselguhr	"	245	3.0	-
7	$FeSO_4$ and Na_2CO_3	without	"	242	0.0	-
8	Ferrous formate and Na_2CO_3	"	"	242	12.0	-

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

Table 50.

Iron Alone, Prepared from $FeCl_2$ by Precipitation with Na_2CO_3.
Various Quantities of K_2CO_3 in the Catalyst

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

The influence of the K_2CO_3 addition does make itself felt just as pronounced as in the case of the copper-containing catalysts. This, of course, only refers to the catalysts which were prepared from $FeCl_2$. With other modes of preparation as will be shown in a later chapter, a subsequent addition of K_2CO_3 can cause a considerable increase in activity. The catalysts precipitated from $FeCl_2$ and containing various quantities of K_2CO_3 require a long time of induction just as the K_2CO_3-free catalysts. The maximum contraction for these catalysts is reached only approximately after 3 weeks of operation, and the yields obtained up to this time do not show any great differences. The

K_2CO_3-free catalyst furnished 22 grams, whereas with the addition of 1/8 percent K_2CO_3, 33 grams, with the addition of 1/4 percent K_2CO_3, 30 grams, and with 1/2 percent K_2CO_3, 25 grams of liquid products per cubic meter of mixed gas were obtained. The experiment temperature in all cases was 240°C., Consequently, it was approximately 10 degrees higher than for the corresponding copper-containing catalysts. After 3 weeks of operation, a further increase in activity was observed in no case.

(Ackermann)

B. Princip~~le~~al Experiments.

1. Dumped weight* and ~~catalytic activity~~ mode of preparation.

a. ~~Mode of preparation and dumped weight.~~

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

a. Precipitation~~s~~:

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

b- Precipitations with Soda:

As may be seen from Tables 51 and 52, the dumped weights vary between 0.26 percent and 1.00 percent. There seems to be a fundamental difference in the dumped weights of the precipitated ferrous catalysts and the precipitated ferric catalysts. The explanation may be that from ferrous salts, at first, ferrous carbonate is precipitated, whereas from ferric salts, ferric oxy-hydrate is formed. This at first voluminous and very difficultly filterable precipitate bakes on

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

drying, and forms a blackish-blue brittle mass. It has an especially high dumped weight.

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

The greatest variation between dumped weights and precipitating conditions occurred with the normal precipitation of the ferrous chloride*. (Table 51, precipitation 5:10).

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

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

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

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

same time, the velocity of crystal growth of the $FeCO_3$ crystals increases. Whereas in the case of the normal precipitations, sufficient chloride ions are present in the precipitation mixture from the very beginning; in the case of reverse precipitation, chloride ions have to be added to the soda solution before the precipitation is carried out.

Table 52.

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

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

c. Precipitations with Potash.

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

d. Precipitations with Sodium Hydroxide.

The precipitations with sodium hydroxide give, in all cases, high dumped weights. The results of these precipitations do not depend on whether ferrous or ferric salts are used. The dumped weights obtained vary from 0.6 to 0.9. It is a known fact that from ferrous salts, at first, a white ferrous hydroxide is precipitated which is very difficult to filter in the presence of ferrous carbonate. By drying, it does not loosen up. On account of the ease with which it can be oxidized after the drying operation, it chiefly consists of ferric oxide. The dumped weights of all the catalysts which appear first as ferric oxide slates depend somewhat on the size of the powder: Powdered by means of a mortar:

10 minutes	15 minutes	20 minutes
0.74	0.61	0.59

2. ~~b~~. Catalytic Investigations of Catalysts With Various Dumped Weights.

We use the contraction as a measure of the activity of the catalyst. An equivalent of 10 grams of iron was used with 4 liters per hour of mixed gas at 240 to 250°C. Table 53 contains the various catalysts arranged according to their increasing dumped weight. Considering catalysts which were precipitated from the same salt, no relationship seems to exist between contraction and dumped weight. The comparison of catalysts prepared from different salts, however, shows that the ferric nitrate catalysts are more active than the ferrous chloride catalysts: High activity decreases for large dumped weights. Small activity decreases with small dumped weights.

Table 53.

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

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

This finding is in contradiction with the opinion that catalytic activity increases with decreasing dumped weight. As a matter of fact, the dumped weight does not seem to give any information on the (inner) catalytic active surface of a catalyst. A better ~~suited~~ means of testing the catalytic properties ~~should~~ would be perhaps the determination of the heat of adsorption which may be readily obtained as the heat of wetting when ethanol is used, for instance. Thus, in accordance with the catalytic results, we found that a catalyst precipitated with soda from ferrous chloride and having a dumped weight of 0.31 exhibits a heat of wetting of only 2.3 calories per ~~one~~ gram of iron, when 96 percent of alcohol was used. The corresponding precipitated ferric nitrate catalyst with the dumped weight of 0.83 had a heat of wetting of 9.4 calories per ~~one~~ gram of iron. Summarily, it can be said that dumped weight determinations are not suited to predict the catalytic properties of iron catalysts. This goes for ferrous as well as ferric salts. Another reason for this is the fact that the catalysts themselves, under the same washing conditions, contain various amounts of foreign material which has been introduced through the precipitation. Later washing experiments showed that the ferric nitrate catalysts mentioned in Table 53 must have contained still considerable amounts of Na_2CO_3. This was probably responsible for the higher activity which those catalysts exhibited when compared to the chloride catalysts.

Table 54.

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

Iron salt	Cat. No.	Precipitant	Dumped weight	Temp., °C.	Max. contraction, percent	Hours of operation
Ferric nitrate	1	NH_3	0.98	240	7.5	84
	2	$(NH_4)_2CO_3$	1.00	235	10.0	120
	3	Na_2CO_3	1.00	235	7.5	120
	4	"	1.00	234	11	120
	5	"	1.00	234	11.5	120

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

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

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

The addition of alkali carbonate has an ~~acts similarly~~ activating influence upon the iron one-component catalysts similar to that ~~than it does~~ upon the multi-component catalysts. In order to study the effect of the alkali, an experiment was carried through for which the alkali was to combine with anions in the catalyst which were believed to be damaging to the catalyst. With this, the function of the alkali would be fulfilled. An excess of alkali in such an instance would even be unfavorable. As the experiment reveals, however, (Table 55), this assumption does not seem to hold because the activity kept on increasing with increasing alkali addition, and it increased independently of the quantity of chloride present which was supposed to interact with the alkali.

Table 55.

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

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

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

b. Excess alkalization and removal of ~~not~~ un-adsorbed alkali quantities by suction ~~respectively~~ and washing, respectively.

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

Table 56

Ferric Nitrate - Precipitated Catalyst, Alkalization and Subsequent Removal of Alkali by Suction and Washing

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

Aside from the finding that the possible adsorption of the optimum alkali quantity which might have taken place on the catalyst was not very permanent as could be seen from the fact that with subsequent removal of K_2CO_3, the activity decreased, this experiment gave some other very important information. Titrating with 1/10 N hydrochloric acid, the filtrate obtained from the washing operation of sample (d) (methyl red), ~~we~~ found an alkali quantity which was three times as large as the quantity of K_2CO_3 added for the purpose of alkalization. The excess alkali can only have originated from the catalyst itself and probably remained there on account of insufficient washing. Hence, the catalyst had been prealkalized by the precipitating soda. From this may be explained without any difficulty the slowly increasing activity of sample (a); the course of the activity increase is characteristic for soda alkalization. Likewise the rapid decrease in activity of sample (b) may be due to over alkalization present Na_2CO_3 and 1/2 percent K_2CO_3.

c. Precipitation in Presence of Fixed Alkali.

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

d. Exhaustivel~~y~~ washing the ferric nitrate catalysts precipitated with soda.

According to experiences made so far with iron one-component catalysts, more active catalysts may be obtained by precipitating ferric nitrate than are obtained by precipitating such ferrous salts as, for instance, ferrous nitrate or ferrous chloride. We have found that the resulting activity is independent of the precipitant. With regard to the precipitant, we found that Na_2CO_3 was superior to $(NH_4)_2CO_3$. According to this, the most active catalyst should be expected to result from a precipitation of ferric nitrate with sodium carbonate. It was our aim to find the optimum alkali quantity which was necessary for such a catalyst. In order to be independent during the determination of the optimum alkali quantity~~, some alkali contents~~ of some residual alkali quantities still present in the catalyst (due to more or less thorough washing of the catalyst), the washing operation of the catalysts was followed up by alkali determinations of the wash water (titration with HCl) ~~so long~~ until ~~xx~~ worthwhile quantities of soda were removed ~~any~~ no longer from the catalyst.

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

~~3.~~ 4. Most Effective Iron One-Component Catalyst.

a. Method of Preparation (normal experiment).

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

~~b.~~ ~~Alkali quantity~~ and catalytic activity.

Alkalization:

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

From Table 57, it may be seen that with increasing alkali quantities, the activity increases. The catalyst containing 1/4 percent K_2CO_3 furnished its maximum contraction ~~already~~ after 4 days of operation; when containing 1/8 percent K_2CO_3, it reached a maximum contraction after 10 days, with 1/16 percent after 5 to 6 days; and without alkali, ~~already~~ after 3 days. The time of in-

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

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

c. Catalytic activity during life-tests.

The experimental results in Table 58 are to be judged as follows: 1/4 percent K_2CO_3: Time of induction 3 to 4 days, more than 50 grams of liquid hydrocarbons up to the tenth day of operation; 50 - 40 grams up to the 22nd; and 40-30 grams up to the 38th day of operation. 1/3 percent K_2CO_3: time of induction, 8 days, more than 40 grams of liquid products up to the 38th day of operation. The average yield between the 3rd and 238th day of operation for the catalyst containing 1/4 percent alkali was 43 grams; for the catalyst with 1/8 percent alkali, it was 44 grams of liquid hydrocarbons. The addition of 1/8 percent K_2CO_3, consequently causes just as good an average yield for 38 days of operation than the addition of 1 [illegible] percent K_2CO_3. Possibly the optimum alkali quantity is somewhere between 1/8 and 1/4 percent.

Table 57.

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

Days of operation	0 percent K_2CO_3		1/16 percent K_2CO_3		1/8 percent K_2CO_3		1/4 percent K_2CO_3	
	Contraction, percent	Liquid products g./m³	Contraction, percent	Liquid products g./m³	Contraction, percent	Liquid products g./m³.	Contraction, percent	Liquid products g./m³
1	8.8	--	13	--	14.6	--	18	--
3	10.4	--	15.5	--	20.8	--	27.7	--
4	10.4	--	18	--	22	--	29.5	--
5	11	11.2	19.6	33.1	24.5	42.5	29.8	55
7	9.6	12.2	22.5	31.3	23	44.1	30.0	54
10	--	--	22.0	38.4	26.5	46.6	28.7	53
14	--	--	20.7	38.1	26.3	45.8	28	47

Table 58.

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

Operating Temperature: 233-235°C.

Days of operation	Catalyst No. 1 Contraction, percent	Catalyst No. 1 Liquid products g./m³.	Catalyst No. 2 Contraction, percent	Catalyst No. 2 Liquid products g./m³.	Catalyst No. 3* Contraction, percent	Catalyst No. 3* Liquid products g./m³
1	14	--	15.8	--	15	--
3	24.5	--	29.3	--	29.3	--
5	25.3	43.5	29.5	51.4	31.8	--
7	26	46.2	28.5	51.2	32.0	54.5
10	26.7	50.6	29.0	47.2	31.2	50.0
14	26.0	46.0	27.0	41.0	31.4	--
17	26.0	42.0	26.2	38.1	30.0	48.3
21	26.5	42.3	26.2	37.6	30.0	45.0
24	27.0	44.7	26.5	37.7	28.7	--
26	--	--	--	--	27.5	38.8
28	--	43.2	--	36.5	--	--
31	--	--	--	--	27	37.2
38	26.3	39.9	21.5	28.3	26.0	33.6

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

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d. Pelleting and Catalytic Activity.

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

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

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

A catalyst which contained 1/4 percent K_2CO_3 and was prepared by precipitating ferric nitrate was allowed to act on mixed gas at 235°C. for 48 hours. The resulting contraction was 24.5 percent. Following this reaction, a mixture of

CO with steam containing both components in the ratio 1:1 was ~~lead~~ led over the catalyst. (Two liters of CO were bubbled through water at 83°C.; the vapor pressure of water at this temperature is 1/2 atmosphere.) In the end-gas, we found 32 percent CO_2 and only 7.3 H_2, whereas the CO contents had decreased by 36.6 percent. According to this, the expansion was only 5 percent. (According to the water-gas generation and assuming a CO_2 formation, an expansion of 32 percent is expected.) Consequently, we are justified to conclude that parallel to the water-gas reaction, the benzine synthesis occurs simultaneously. If one assumes that one CO_2 is formed from approximately $2CO + 1H_2$ at conditions of the benzine synthesis, one is in a position to calculate approximately the original water-gas conversion. According to this, ~~around~~ 20 percent of the CO was converted with water. After 24 hours, the CO_2 decreased to 20 percent, whereas the expansion increased simultaneously up to 9 percent. We conclude from this that the benzine synthesis had decreased more rapidly than had the water-gas reaction. At the same time, we found that one gram of yellowish oil had collected in the receiver. After switching to mixed-gas, the catalyst at first gave 13 percent contraction; 48 hours later, it gave 28 percent contraction; and again produced colorless oil.

We have found that the iron one-component catalyst at synthesis temperatures is in a position to shift the water-gas equilibrium towards the CO_2 direction. This discovery, however, is not yet sufficient reason and does not give sufficient basis for explaining why the benzene synthesis takes a different course over the iron one-component catalyst than it does over cobalt and nickel catalysts.

~~4~~ 5. Regeneration Experiments.

a. With H_2 at Synthesis Temperature.

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

b. With Super-heated Steam at Synthesis Temperature.

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

c. Oxidation with Air at Synthesis Temperature.

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

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

6. ~~5.~~ Alkalization with Sodium Carbonate.

The alkalization with 1/8 percent, 1/4 percent, and 1/2 percent of sodium carbonate yielded a smaller activity than with the corresponding potassium carbonate experiments. The times of induction are longer. After approximately 8 days of operation with 1/4 and 1/2 percent Na_2CO_3, maximum contractions of 23, respectively 28 percent were obtained. The maximum yield for a catalyst containing 1/2 percent Na_2CO_3 was 45 grams of liquid hydrocarbons after 8 days of operation. It is remarkable to observe that the catalysts alkalized with potassium carbonate retained their activity for a longer period of time. After 42 days of operation, the catalyst containing 1/2 percent Na_2CO_3 still yielded 40 grams of liquid hydrocarbons; the one containing 1/4 percent Na_2CO_3, after the same length of time, gave still 36 grams of liquid hydrocarbons. For both catalysts, however, the oil was yellowish in color. At this point we want to mention a catalyst for which we observed the longest time of operation ever obtained for an iron one-component catalyst. We are talking about a ferric nitrate catalyst precipitated with soda which was, however, not washed exhaustively. (See Table 56, test a) This catalyst was not alkalized after the washing operation. However, the water from the washings showed that at least 1/2 percent Na_2CO_3 was still contained in the catalyst as residual alkali originating from the precipitation. It reached its highest contraction only after 20 days of operation (27 to 28 percent, maximum yield, 46 grams), and between the 8th and 42nd days of operation, gave more than 40 grams of liquid hydrocarbons. On the 58th day of operation, the contraction was still 23.5 percent, and the yield 38 grams.

~~6.~~ 7. Multi-component Catalysts which were Precipitated in the Same Manner as the Best Iron One-component Catalysts.

a. Iron-Copper Catalysts.

Stimulated by the good results with iron one-component catalysts, it was suggested to find out what influence the presence of copper would have on the best iron catalyst. It appeared to us that a further increase in activity should not be impossible. As the experiments show, however, no improvement but rather a deterioration resulted. We precipitated ferric nitrate-copric nitrate solutions in the same manner with soda as we precipitated the iron salts from which the pure iron catalyst was made. The copper quantities used were one percent copper, 5 percent copper, and 20 percent copper. For the first series of experiments, catalysts were used which were not alkalized.

In the course of 7 days of operation no effect of the copper could be determined. All three catalysts behaved exactly as did the copper-free iron catalysts; the contraction was around 10 percent at 235°C. In a further series of experiments, the catalysts were alkalized with 1/4 percent K_2CO_3. The contraction went up to 27 to 28 percent independent of the copper quantity. The yield of liquid hydrocarbons was, in the best case, 49 $g./m^3$. After 24 days of operation, the products formed were yellow ~~already~~ at an average contraction of 26 percent and 38 grams of yield.

b. Iron-zinc-oxide Catalysts.

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

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

8 ~~7.~~ Ferric Nitrate Decomposition Catalysts.

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

As starting material, we used the ferric nitrate solution, which we have resorted to before, when preparing the precipitated catalysts. It was evaporated to the consistency of a syrup (partial decomposition). Through some preliminary experiments, we found that the catalyst is more active the faster the decomposition occurred. Therefore, the thickened nitrate solution was rapidly decomposed by introducing small portions into an iron pan heated directly. It was stirred continuously until the evolution of nitrous oxide fumes almost ceased. The red-brown oxide was immediately removed from the hot pan. The best catalysts were obtained when alkalization was carried out before the decomposition. The alkalization was accomplished by adding the calculated quantity of potassium carbonate to the nitrate solution. With 1/4 percent K_2CO_3 and at 235°C., a contraction up to 29 percent was reached and 48 grams of liquid hydrocarbons per cubic meter of mixed gas were formed. It did not matter whether the catalyst was powdered or whether it was used in small pieces, such as were obtained after the decomposition. As compared to the precipitated catalysts, a faster decrease of activity is noticeably because after 13 days of operation, the contraction had decreased to 25 percent and the yield to $38g./m^3$

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

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

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

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

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

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

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

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

d. Paraffin Extraction from Iron Catalysts.

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

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

(Meyer)

Table 59

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

Exp. no.	K_2CO_3 contents, percent	Days of operation	Consumption of mixed gas per m³	Extraction of paraffin in grams	Paraffin in g./m³ of mixed gas	Contraction	
						percent	after days
1	0	50	5.0	4.5	0.9	20	42
2	1/16	60	6.0	6.5	1.1	23	42
3	1/8	60	6.0	7.8	1.3	26	42
4	1/4	55	5.5	10.1	1.8	26	42
5	1/2	20	2.0	10.0	5.0	18	21
						7	32
6	1	10	1.0	12.0	12.0	6	9
7	2	7	0.7	8.2	11.7	7	4

Table 59 gives information about the paraffin quantities contained in iron catalysts with varying amounts of K_2CO_3. This data is for a definite period of operation. The third last column indicates the quantity of paraffin which was obtained from the catalyst by extracting it with synthetic benzene (fraction 80-100°C.). The quantity of paraffin given there is given as grams per cubic meter of mixed gas put through the unit. The catalyst with 1/4 percent K_2CO_3 contained approximately twice as much paraffin as did the catalyst which contained no K_2CO_3. A catalyst containing 1/2 percent K_2CO_3 after being in operation for 20 days, had already taken up the same quantity of paraffin as did a catalyst containing 1/4 percent K_2CO_3 after 55 days of operation. Still larger paraffin quantities are contained in the catalysts alkalized with one percent, ~~respectively 2~~ and two percent K_2CO_3. The decrease of activity of the catalysts increases with increasing paraffin formation (last column). ~~To this~~ It should ~~should~~ be ~~added~~ noted, that the decrease of the activity does not depend on the quantity of the paraffin taken up by the catalyst, but rather depends on the simultaneous appearance of decomposition products of the paraffin. These decomposition products show up in a more pronounced way in the case where heavily alkalized catalysts are used. For the catalysts containing little K_2CO_3, the appearance of the decomposition products does not set in as early.

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

(Bahr) c. Acid Products.

Just as in the case of cobalt catalysts, so also with iron, not only benzene, oil, and paraffins are obtained, but small quantities of acid products as well. When the synthesis is carried out with carrier-free catalysts, these acid products are chiefly found in the oil; but also to some extent in the paraffin which can be extracted from the catalyst. Such acid products may be obtained from the catalysts almost immediately if the catalyst is boiled with a one to 2 percent normal Na_2CO_3 or NaOH solution. One then obtains quickly colored yellow extracts which after an acidifying extraction with ether and evaporating off the ether, leave behind semi-liquid products of pungent odor which reminds one of the higher fatty-acid series. In one case we obtained 0.5 grams of such acid products after extracting 40.5 grams of a catalyst having served for some time, that is, approximately one percent of the catalyst weight. Perhaps the activating alkali contents of the catalyst gradually enter~~s~~ into reaction with the acid products and form~~s~~ soaps. It is possible also that to a lesser degree fatty-acid salts of iron, copper, and manganese might appear. In this connection, an older experiment is of interest during which the used-up catalyst, after the paraffin extraction, was treated with sulfuric acid. When extracted with benzol, the catalyst gave 9 percent paraffin as referred to the catalyst weight. In order to remove some ether soluble products, which might have still been present in the catalyst, it was boiled out with ether, and thereafter it was refluxed with dilute sulfuric acid. When the acid was added, almost violent CO_2 evolution occurred. After filtering off the insolubles, the sulfuric acid solution was extracted with ether in the perforated funnel and the insoluble residue from the catalyst was boiled out with ether as well. Both extractions were combined, and after evaporating off the ether, the combined residue amounted to 1.2 grams of a liquid product in which small solid particles were dispersed. The whole mass had a pungent odor. Referred to the final weight of the catalyst, approximately 9 percent paraffin was obtained and 4.4 percent "acid products".

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

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

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

XVII. Advantages and Disadvantages of Iron Catalysts.

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

1. When iron catalysts are used, we do not have to rely on the expensive and rare cobalt, but can use instead, the cheaper iron which is available in Germany in unlimited quantities. An addition of expensive thorium is not required. The preparation of the iron catalysts can be carried out technically in the same type of apparatus as the cobalt catalyst ~~is prepared~~, that is, either by dissolving iron in nitric acid or hydrochloric acid. For the precipitation in both cases, soda may be used.

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

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

4. The fatigued iron catalyst may be regenerated by a simple treatment with air (after previous extraction). By doing so, it regains its old activity. This is quite contrary to cobalt catalysts.

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

6. The products of the iron catalysts (benz~~e~~ine, oil, and paraffin) are qualitatively the same as in the case of the cobalt catalysts. The iron catalyst offers the possibility to produce benz~~e~~ines with a high content of unsaturates.

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