Ammonia Laboratory

June 1947

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The Hydrocarbon Synthesis from Carbon Monoxide and Hydrogen

Researches of the Ammonia Laboratory from 1935 - 1944

Researches of the Oppau Ammonia Laboratory in the Fischer-Tropsch Synthesis

I. Investigations with Cobalt Catalysts

a. Experiments at Atmospheric Pressure

The Ammonia laboratory started its investigations in the f of pressureless hydrocarbon synthesis according to Fischer-Tropsch i by setting itself the task of reexamining the relevant material in t literature. Dr. Lorenz was able to prove by numerous experiments th when the cobalt-thorium-kieselgur and nickel-manganese-aluminum-kies catalysts proposed by Fischer were used, the values checked in respe performance and life of the catalysts, type of product, and suscepti of the synthesis to temperature and catalyst poisons. He further de that there was little choice in the individual products so that a si adaptation to market conditions, i.e., a purposeful shifting in the position of the product, was not possible. It was possible, for exa to roughly triple the paraffin proportion only by a substantial incr of the contact time of the gas with the catalyst to about 6-7 times technically conventional period at a synthesis temperature kept down 160-170 degrees. This was only possible at the expense of the catal life. But even this short-lived success was dependent on the type o kieselgur used, for other types, even under these extreme conditions did not give these high paraffin yields without some restrictions on the kieselgur. When the kieselgur was replaced with silica gel, the formation of higher-boiling products was greatly impaired. The repr ibility of the catalysts remained unsatisfactory despite expenditure time and effort. Statements on the influence of experiment variatio cannot be made with any certainty until this indispensable condition is met.

The author, together with Dr. Meisenheimer, in October 1936 undertook to continue the investigations at this juncture. In this connection it seemed advantageous to examine the part played by the individual components of this catalyst by temporarily restricting ourselves to catalysts containing cobalt as the basic metal. In order to proceed gradually a cobalt catalyst was produced at first without additions in order to check on the influence of various precipitation conditions, reduction temperature, and alkali content. The result of the initial investigations, whose success is attributable to our close collaboration with the X-ray laboratory, can be summed up as follows:

1. Pure cobalt metal produced under specific precautionary measures, with a catalyst space velocity of 1 liter gas/1 gram Co hourly, yields approximately 110 grams/Ncbm synthesis gas as compared to 25 grams/Nm^3 in the gasoline synthesis. This is the value given in the literature. e lower the reduction temperature the better the catalytic activity of these catalysts without promoters or carriers. Catalytic activity does not occur at high reaction temperatures due to premature sintering.

2. However, if the finished catalyst contains noticeable quantities of Co_3O_4 along with basic carbonate before reduction, it will be substantially less susceptible to the reaction temperature as a result of the difficulty of reducing this oxide, which acts as a stabilizer.

Red. Temp.	grams yield/m^3	
	without	with
	Co_3O_4	
350	0	30
300	1	-
270	15	108
225	39	135

3. The following was proved to be reliable as a catalyst production recipe:

Cobalt nitrate containing water of crystallization is dissol in water and, with a little more than the calculated quantity of potas carbonate, subjected to a cold drop by drop precipitation within 40-50 hours. The precipitation is washed out by a suction filter until ther no longer any evidence of nitrate in the filtrate. The moist catalys is dried for 24 hours at 110 degrees and, in order to attain a suffic centent of Co_3O_4 by the oxidation of CoO, again moistened and again d at 110 degrees for 10 hours. The catalyst is reduced at 225 degrees. Time about 10 hours.

4. The recrystallation which rapidly set in caused a short for this unstabilized catalyst.

5. Carbide formation in the spent catalysts could not be c with X-rays.

At the time that this information was discovered a new prob was added, namely, the increase of the paraffin yield. This task wa closely connected with the work being done at Oppau in the field of paraffin oxidation to soap-stock fatty acids, or wax. As a result o this we were forced to pursue our activities in several directions w frequently intersected.

The simplest manner of stabilizing cobalt obtained in an a form was deposition on carriers. For this purpose we initially used kieselgur, the extreme case simultaneously occurring in which we for once used a Fischer catalyst with a thorium content of 0. This res in a catalyst which naturally did not quite approach the standard F catalyst with its 18 per cent thorium in respect to activity, but w displayed an excellent life. It was used about 4 months without being regenerated. This was attributed to the fact that it only formed paraffin at the start; later, after about 14 days, practically no more paraffin was formed. This direction, however, did not conform to our wishes, but at least it showed us the part played by one of the three components, the thorium oxide.

It accomplishes two functions in the catalyst combination: 1. Stabilization of the catalyst in an active form, which is only possible otherwise by a special drop by drop precipitation. 2. Guiding the synthesis into the production of long-chain products. This information led us to investigate catalysts with a high content of thorium oxide for the purpose of an increased paraffin yield. As was to be expected, an increased percentage of paraffin was obtained. However, since the total yield in conjunction with the greater thorium content, at first drops slowly, then more rapidly, the actual increased yield of paraffin may be ignored. However, the combination of a thorium-rich and a normal catalyst in a two-stage operation proved to be good. The use of this catalyst resulted in a paraffin yield of 35 grams/Ncbm of a total yield of 130 grams/Ncbm. The experiment lasted 2 months, hydrogen regeneration at 220 degrees occurring after each 14 days. The experiment was discontinued after two months without any visible falling off of activity. Further efforts were made to increase the paraffin contents by the pressureless procedure. Alkalization of the catalyst or modification of the gas composition (increasing CO content) were tried. It was shown that each individual measure or a combination of both tended towards increased paraffin formation. However, this increase only reached moderate proportions and does not compare with the increase attained by raising the thorium content. Since a decrease in the total yield is tied up with these measures, the increase in the percentage of paraffin is no yardstick for the actual formation of paraffin.

However, all these efforts to achieve an increased yield of paraffin are outstripped by another measure, namely, the application of pressure. It is therefore not necessary to go into the above experiments in greater detail. However, before turning to these pressure experiments we should like to report briefly on our efforts to find other promoters and carriers for the promotion and stabilization of the cobalt.

At first magnesium oxide seemed to us to be a suitable promoter addition since it forms a spinel with cobalt oxide (Co_2O_3), and forms an unbroken series of mixed crystals with CoO. Because of the attainable homogeneity this appears to us to be a favorable precondition for catalyti activity after the reduction. It was determined as a result that addition of 2-15 per cent MgO without addition of kieselgur were approximately equivalent among each other, but gave a total yield of only about 80 grams This type of catalyst is very dense and, since it possesses a higher metal content, with respect to the same quantity of metal, it occupies a substantially smaller volume than the kieselgur catalyst; for example, 4 grams of cobalt are contained in 10 c.c., it would otherwise require about 40 c.c. This results in a four-fold volume space velocity since the catalyst charg rate is referred to the gram quantity of cobalt (1 liter/1 gram Co/hour). However, if it is desired to employ the usual volume charge with the catal then four times as much catalyst metal is needed and a yield of 100 grams/ is obtained after two months without regeneration. This corresponds to th life of the usual cobalt-thorium-kieselgur catalysts.

The attempt to deposit the cobalt-magnesium catalyst combination on kieselgur resulted in a catalyst with a yield about 10 per cent poorer than the standard catalyst with a similar paraffin yield.

Further investigations on the replacement of magnesium oxide by manganese, ceric or lanthanic oxide resulted at best in equivalent but not better catalysts than those proposed by Fischer.

The cobalt-nickel-manganese-uranium-kieselgur catalyst proposed by the Japanese, with the same yield as the standard catalyst, is quite noteworthy because of the marked direction of its reaction towards paraffin (28 grams paraffin/Ncbm in over four weeks). On the basis of our own experiments we attribute this condensing property to the influence of the uranium.

Although we do not ignore the good catalytic properties of the standard catalyst we received the impression during our investigations that the kieselgur might easily lead to trouble. The fault lies in the undefined character of the material since we have not reached a point where we can exactly analyze its make-up. Its physical structure is doubtless of importance along with its chemical composition so that, in the end, only catalytic experimentation can decide upon its utility. We therefore spent a great deal of time in looking for another material to replace kieselgur, such as aluminum oxide, kaolin, magnesium oxide, silica gel, talc, porcelain, etc. Our experiments showed that kaolin and aluminum oxide, after a pre-treatment with temperatures of 400-600 degrees or 800-1000 degrees, yield a catalyst practically equivalent to the kieselgur catalyst (life four months), all other carriers reacting unfavorably. Nevertheless, the fact that we retained the kieselgur in general is.explained by the observation that a less favorable type (4 S) was substantially improved by igniting in a current of air at temperatures of 500-700 degrees. It even outstripped type 20, the type generally employed by Fischer which was supplied by the German Kieselgur-Werke, Hanover after treatment by ignition. The treatment at Hanover, however, does not occur at a specific temperature, many particles therefore being overburned. A further observation was made to the effect that if slight additions of magnesium oxide are added to the kieselgur to the extent of 1-2 per cent with respect to the cobalt metal, fluctuations in the behavior of the various kieselgurs could be practically eliminated. Nevertheless, experiments undertaken from time to time with the aim of replacing kieselgur with silica gel finally achieved success by the observation that a silica gel preheated for about five hours in a current of air at 800 degrees to avoid silicate formation can completely replace kieselgur if a fine-pored gel is employed.

We can summarize the results of our numerous experiments by stating that we cannot propose a more serviceable catalyst than the cobalt-thorium-kieselgur catalyst. We consider of equal value for synthesis performance the slowly precipitated thorium-free Co catalyst with about 1 per cent Ag on fine-pored silica gel which offers the advantages of a saving of thorium, of reproducibility in the synthesis reactor, and of better catalyst life. The weaknesses of the thorium-containing standard catalyst lie in the fact that it contains kieselgur with its unpredictable qualities and that its reproducibility is still somewhat uncertain. The fluctuations in the kieselgur, however, can be equalized by the addition of slight quantities of magnesium oxide and by heat pre-treatment at a specific temperature that is not too high. Reduction in receptacles other than synthesis reactors is also technically objectionable. Transporting the reduced catalyst under carbon dioxide causes the most active spots to be lost as a result of surface oxidation. Therefore we consider the addition of about 1 per cent of silver to the cobalt catalyst to be one of the advantages of our procedure. The reduction temperature is thereby lowered so far that we can reduce directly in the synthesis reactor without the necessity of taking a decrease in the yield as is the case with copper. In conclusion, the following experiences gleaned in catalyst preparation may be mentioned:

Potassium bicarbonate was proved to be better than potassium carbonate as the precipitating agent for the Fischer catalyst that was quickly precipitated and subsequently boiled since the catalysts become more active and more readily reproducible. On the other hand, potassium carbonate must be used for the thorium-free catalysts since these catalysts are slowly precipitated without subsequent heating. Under these circumstances a complete precipitation cannot be achieved with bicarbonate.

Furthermore, washing with a minimum quantity of wash water was proved to be necessary for otherwise, despite freedom from alkali, less active catalysts would be obtained.

We know from experience that the size of the excess of precipitating agent is of negligeable importance. A direct relationship of catalyst efficiency with the pH of the precipitation was not noticeable. The type of drying, whether in air at 110 degrees, in a current of carbon dioxide, or in a vacuum, is equally unimportant.

b. Experiments with Medium Pressure

As was already mentioned, the synthesis conducted under a slightly increased pressure brought about a substantial improvement in the paraffin yield. Nevertheless, more than a year's work was necessary before the technical development of the laboratory apparatus had reached a point where we could obtain with certainty a total yield of 130-140 grams/Ncbm with a paraffin proportion (boiling point above 320 degrees) of upwards of 60 per cent.

The pressure used by us in the laboratory pressure experiments ran from 12 atmospheres to a maximum of 20 atmospheres; no difference in paraffin production was found within this pressure range. The charge velocity was the same as in the pressureless experiments: 1 liter gas/ 1 gram metallic cobalt/hour. Experience shows that our procedure for attaining the highest possible paraffin yields with cobalt-kieselgur catalysts free of additions, which almost stopped producing paraffin after several days without pressure, turned out to be more reliable than the thorium-rich catalysts which are good paraffin producers withou pressure. Catalyst life was also satisfactory; after ten weeks of operation the catalyst still retained more than 90 per cent of its maximum activity. The explanation for the inferiority of the thorium-containing catalysts under pressure to the catalysts free of thorium is based on the fact that the former forms very high-molecular weight paraffin which leaves the catalyst to a lesser degree and therefore leads to the block of the active spots.

The most important innovation in the experiments was the inst lation for the first time of pressure flow manometers which permit exac measurement under pressure of the even flow of the smallest quantities gas (e.g., 12 liters of depressured gas/hour = 1 liter gas/hour at 12 a mospheres). The requisite pressure capillaries with fused manometer le were made from special Jena glass. The connection to the high-pressure piping was accomplished by means of stuffing boxes fitted with special soft rubber packing. The pressure flow manometers constructed in this manner withstood a test pressure of 20 atmospheres, the glass and metal joints being found sufficiently tight. The pressure capillaries were tested by putting the entire apparatus under pressure after installation before the start of the experiment. Then through an analysis valve behind the synthesis reactor a constant volume of gas, e.g., 12 meters/hour, was let down through a flow manometer. After a little while the proper manometer level could be read off on the pressure flow manometer. The constancy of the result was tested by repeated readings over a period of time. Varied volumes of inlet gas under pressure can be accurately gaged by adjusting the quantity of exit gas. The corresponding quantity of let down gas is then stated to be the inlet gas volume. Comparison of the inlet gas volume calculated by m of the oxygen balance with the inlet gas volume measured by flow capillaries demonstrated that measurement of the inlet gas volume under pressure was far superior in most instances to calculation of the inlet gas volume. An additional advantage lies in the fact that a more uniform operation of the reactors can be attained by keeping the inlet gas volume constant with the pressure capillaries.

Later operation showed that a by-pass in the inlet gas capillaries was advantageous. By cutting off the narrow capillary path it enables the product to be forced out of the pressure separator without risk, and makes possible an easy interchange of capillaries without interrupting the inlet gas feed. This was very convenient when the pressure capillaries were gaged during operation.

A brief survey of the performance of cobalt-kieselgur-catalyst employed by us, which was prepared by slow drop by drop precipitation of a cobalt nitrate solution in the cold with potassium carbonate, will be given in the following in order to facilitate a comparison with the iron catalysts developed by us at a later date for the carbon monoxide-hydrogen synthesis. In general the precipitation lasted for more than 24 hours. Catalyst life lasts for several months so that regeneration with hydrogen seldom comes into question.

In the following we give several values obtained by various methods of preparing our catalyst:

Expt. no.	Cat. no.	Temp. °C.	CO consum.	in exit % CO_2	gas %CH_4	% K_2O/grams cat. for 100 Co	Yield solid + liquid product/Nm^3	% Par. >320	% Str. chain

(Table on page 148)

186° 71 1.0 7.7 = 0.324 kg/liter Kt/day

appear as mean values 135 61 98

Division of the primary product into boiling ranges

(Table on page 148)

Mean values

If a lower yield is desired, especially if only one synthesis reactor is available (technically the process is run in two stages) then it is possible to manage with lower temperatures:

Experiments with a lower CO conversion (charge velocity as usual 1 liter/1 gram Co)

Expt. no.	Cat. no.	Temp.	CO consump.	in the exit gas		% K_2O in catalyst 100 Co	grams yield solid plus liquid prod./Ncbm
				% CO_2	% CH_4		

(Table on page 149)

Mean values:

It can be seen that the methane content is still proportionately high even with this slight CO conversion. This is attributed to the good hydrogenation power of the cobalt. One would think therefore that the catalyst could be adjusted to another cobalt concentration by kieselgur, thereby possibly checking the hydrogenating influence of the cobalt. However, this was not successful, as is shown by the following table:

Expt. no.	Cat. no. Content		Temp.	Co consump.	%CO_2	%CH_4	grams yield of solid plus liquid prod. Ncbm	% par. > 320°	% straight-chain
	%K_2O	%Co			in the exit gas				

(Table on page 149)

There are no regular great differences, in particular the methane content shows no progression of values. There is a progression in the case of paraffin production which increases with rising Co content, whilst, as is evidenced by the boiling point figures, the proportion of hard paraffin rises.

(Table on page 149)

The following series of experiments answers the question: what effect does alkali in the catalyst have on methane formation ?

Expt. no.	Cat. no.	% K_2O/ cat.	Temp.	CO consumption	%CO_2 %CH_4 in the exit gas	g. yield solid plus liquid pr. Ncbm	% Par. 320°	% stra chain

(Table on page 150)

It is evident that with a rising proportion of alkali the synth temperature must be markedly increased to produce the same CO conversion. This, however, assists in the formation of methane, as can be seen from t corresponding values. At the same time it diminishes paraffin formation. This remains even with a decreased CO conversion:

(Table on page 150)

In conclusion, let us offer one more comparison; the behavior o a cobalt catalyst with a $CO:H_2 = 1:1$ synthesis gas. All other experiment were conducted with a $CO:H_2 = 1:2$ synthesis gas:

(Table on page 151)

The table shows: at 1:1 there is a smaller yield of primary product, a higher proportion of olefin and alcohol in the primary product, less straightchainedness of the paraffin, and also less methane formation. In the case of synthesis gas 1:2, methane content diminishes in the course of time if the catalyst is kept at the same temperature. This being the case, it is important in evaluating the methane value to know at what time the sample was taken:

(Table on page 151)

II. Investigations with Iron Catalysts

a. Experiments at Atmospheric Pressure

As a result of the external circumstances caused by the start of the war in 1939 the experiments which were being conducted to synthesize hydrocarbons from carbon monoxide and hydrogen with iron catalysts, which heretofore had been of subordinate interest and had been undertaken in a modest way in connection with cobalt catalysts, became of major interest. Since subsequent investigations were conducted exclusively under medium pressure, the experiments which were conducted previously at one atmosphere will be briefly presented here.

Since we were dealing with what amounted to a new field of activity, the experiments must be evaluated in the light of an initial exploration in the field of catalysts, especially in view of the fact that many questions still remained unanswered. However, this field did not appear urgent enough to devote more work to it. It became quite clear to us even in the early part of our work that it would not be possible, without intensive and systematic work, to develop an iron catalyst capable of completely replacing the cobalt catalyst in the atmospheric pressure process.

The catalysts investigated for the most part consisted largely of mixtures of the following constituents: iron-copper-alkali with magnesium oxide or with aluminum oxide.

Since the copper, according to our viewpoint at that time (future data on the role of the copper will be given later) served solely to facilitate the reduction of the iron, i.e., to lower the reduction temperature, it was present in all catalysts in the constant ratio of $Fe:Cu = 4:1$.

Both catalyst combinations were investigated for the most favorable combination of alkali and metallic oxide, as well as their behavior with respect to variation of the CO:H$_2$ ratio in the synthesi gas and response to the reduction temperature. It was found that, ev under the most favorable conditions of composition and experiment con at best yields of 60 grams of solid and liquid products/Mcbm synthesi gas were obtained over several weeks. Contrasted with this were yiel of about 130 grams/Mcbm with the cobalt standard catalyst (with thori Of the remaining investigated catalyst combinations only two more ser will be stressed. The first aimed at progressive replacement of the cobalt by iron in the cobalt-kieselgur catalyst customarily employed us. In the second series, several iron-nickel (1:1) - aluminum oxide catalysts with assorted methods of preparation were the object of our investigations.

The first series demonstrated that cobalt-kieselgur catalys containing up to 40 per cent iron, with respect to the cobalt, eviden good effectiveness, the yields, however, decreasing as the proportion iron rose. At the same time the optimum synthesis temperature rose. content of cobalt was controlling in the reaction. This is inferred the fact that only water was formed as a by-product during the reacti whereas iron catalysts give carbon dioxide for the most part.

The catalysts of the second series, iron-nickel catalysts, promoted with 5-15 per cent aluminum oxide, gave yields of about 80 g of solid and liquid products, falling far short of the normal cobalt catalysts. The type of precipitation for these catalysts is of littl importance with respect to the total yield; however, it is possible obtain catalysts by slow reverse precipitation (letting the nitrate solution of the metals drop into the potassium carbonate solution) in the cold which are characterized by an extraordinarily small bulk weight as compared with catalysts produced by other means (0.2 and 1.1). Great economies of metal can be effected with the same catalyst space without influencing the yield. In addition to the economies in metal there is still another advantage, namely, that they are easy to use because of their slight sensitivity to temperature. With such catalysts the reaction proceeds mainly in the direction of water formation. In essence this points to action on the part of the nickel which is neutralized by the addition of the iron.

The catalysts with high and low bulk weights are clearly differentiated from each other with respect to their external characteristics. The heavy catalysts are compact, vitreous, dark-brown; the light ones, on the other hand, are light-brown particles which display a tendency toward decomposition as a result of their soft, loose structure.

So much for the experiments with iron catalysts in synthesis at atmospheric pressure.

b. Experiments with Iron Catalysts at Medium Pressure

The aim of these investigations was the synthesis of a paraffin (boiling point, straight chained, iodine number) suitable as a starting material for paraffin oxidation. The problem, therefore, consisted in finding a suitable catalyst capable of replacing to a great extent the cobalt catalyst developed for this purpose by us. This catalyst was to be produced from native raw materials or from raw materials abundantly available to us.

It is not necessary to discuss details of equipment at this poi since the reactors were the same as those employed for the pressure exper ments with cobalt catalysts. It should again be stressed that we are des ing here with small scale experiments, using catalyst charges of 30-100 c

The working pressure - insofar as the contrary is not expressly stated - was always 12 atmospheres since we attained the best results at this pressure with the cobalt catalysts. The catalyst charge rate was nc based on the weight of the metal of the catalyst, as was the case with th cobalt catalysts, but on the volume, and in general, was 240 parts by volume of synthesis gas ($CO : H_2 = 1 : 2$) : 1 part by volume of catalyst/ hour. Since we were more or less concerned with catalyst testing in thes investigations carried out solely on a laboratory scale, we ran only one operating stage, seeing to it that the gas was extensively converted (app. 70 - 80 % consumption). We were quite clear about the necessity for a process of several stages or of recycle operation in conversion to a commercial scale. It was also clear to us that a $CO : H_2 = 1 : 1$ synth gas was more advantageous for iron catalysts if care was taken to see tha if such a gas mixture was used, the conversion proceeded in another ratic up to $CO : H_2 = 1.6 : 1$.

Catalyst Tests

The point of departure for our catalyst investigations was the experience obtained with cobalt catalysts, namely, that catalysts yieldir the least possible paraffin in the pressureless synthesis behave especial well in the medium pressure synthesis in regard to paraffin yield, synthe sizing a great deal, but not an excessively, hard paraffin which leaves the reactor without difficulty and permits undisturbed operation for mont without regenerating the catalyst.

The initial pressure experiments (December 1939) with a promoted precipitated catalyst in connection with the pressureless experiments conducted with it show that it is possible with iron catalysts, too, in principal to obtain a satisfactory, straight-chained paraffin suitable for oxidation to fatty acids which would be equal in quality to the good products obtained with cobalt catalysts. The same total yields and paraffin yields, however, were not attained.

The catalyst used was obtained by precipitating an iron-copper-aluminum oxide-potassium catalyst drop by drop for 48 hours, and was used without carriers. Its reaction temperature ranged from 210 to 220 degrees, viz., within the temperature range up to 230 degrees, which is the maximum allowable for commercial reactors with steam cooling constructed for the synthesis with cobalt catalysts.

Using numerous individual observations, the catalyst combination used in the initial experiments was worked up into a catalyst which fulfilled our requirements in regard to paraffin yield to a large extent. Its composition is roughly equivalent to the following parts by weight: Fe - Cu - Al_2O_3 - K = 100 - 25 - 100 - 10.

Such catalysts were used by us for months at a time always at the same reaction temperature of 208 degrees, the longest run being 135 days, without showing any signs of fatigue at the end of this period. However, after several weeks the paraffin content in the primary product dropped from about 60 to 45 per cent in favor of the gasoline fraction.

The involved method of preparation of this catalyst may be considered a disadvantage. Not merely the two-day precipitation, but also the difficulty of washing the catalyst free of alkali, or of establishing the desired alkali content, requires a great deal of time and care. Therefore, after obtaining good results with magnesium oxide instead aluminum oxide, it occurred to us to test this promoter, too, in our precipitation catalysts at medium pressure.

The influence of various quantitative ratios upon one anoth was investigated in a large number of experimental series. This was at first with catalysts without carriers. Certain regular patterns became evident; however, certain catalysts, after a temporarily good start, revealed an early drop in activity after a lengthy run. This difficulty, however, could be eliminated with the use of carrier catalysts, kieselgur proving itself to be very reliable as in the cas of the cobalt catalysts. In the case of these catalysts, too, the in dual constituents were compared to each other. At the conclusion of these investigations in paraffin synthesis two catalysts were availab which, by way of comparison, showed the following numerical values:

(Table on page 152)

The table shows that there are certain differences, even th they are not very great, in the results attained with these two catal The catalyst promoted by MgO behaves somewhat more favorably with res to the total yield of solid and liquid products in a once-through gas operation. However, this advantage is counterbalanced by the fact th it tends toward the formation of higher-boiling products as a result the higher synthesis temperature. Also, the straightchainedness of t paraffin obtained with it is not quite as good as that obtained with paraffin produced by aluminum catalysts. It was finally possible to eliminate these disadvantages of the magnesium catalyst by producing catalysts, by a high gas throughput during reduction with hydrogen or synthesis gas (5000:1) at temperatures of 180-250 degrees, which required a working temperature reduced by 15-20 degrees as compared with the previous temperature.

We have the following working hypothesis for this catalyst behavior during running in: The conversion of carbon monoxide and hydrogen is not a simple process. Both polymerization and hydrogenation are probably involved, both types of reaction certainly not being accelerated by the same promoters. Furthermore, it is assumed that the methylene group, which is the precondition for polymerization, is formed by the hydrogenation of iron carbide, whereas the hydrogenation of this methylene group to methane, or the hydrogenation of a longer unsaturated hydrocarbon to the corresponding saturated hydrocarbon, proceeds by way of the metallic iron points. The extent of probability whether a formed methylene radical will be hydrogenated to methane, or whether it will have the opportunity to combine with other radicals to form larger complexes, will depend on the metal:metallic carbide ratio. The lower the temperature, the greater the tendancy towards chain formation. The catalyst must also be run in in such a manner that the iron will be in a condition - reduced or unreduced - capable of forming carbide at low temperatures when the carbon monoxide and hydrogen come together, i.e., the synthesis must be capable of completion at low temperatures. The probability is thereby created for an increased yield of paraffin and a smaller loss through undesired gas formation.

The mean values obtained with catalysts promoted by M_gO with different types of reductions (synthesis gas $CO:H_2$ = 1:2, catalyst space velocity 240 liters/liter catalyst/hour) are given in the following in order to make possible a quantitative comparison:

Gas	Reduction Temp.	Charge	Time	Synth. temp.	CO consump.	Grams solid and liq. prod.	% Par. >320° C.	Grams CH Ncbm
without reduction.								

(Table on page 153)

The table shows that the synthesis temperature for catalysts without previous reduction, or reduction at high temperatures, is practi the same, whereas a so-called "flooding" with hydrogen or synthesis gas low temperature makes possible a reduction in temperature. Despite the higher working temperature, however, the unreduced catalyst, insofar as its catalytic activity is concerned, behaves in a manner much more simil to the catalyst reduced at low temperature in regard to the consumption of $CO:H_2$, and the formation of methane, olefin and alcohol, than to the catalyst used at the same temperature, but which was formed at a higher reduction temperature. This supports the conclusion that the iron newly obtained from the oxide is particularly capable of forming the necessary carbide with the carbon monoxide of the synthesis gas, more readily, in fact, than a reduced but already sintered iron. Even though the purpose of this running in is to create an especially reactive iron or iron oxide we are not saying that the iron oxide of the starting material must be thoroughly reduced. On the contrary, certain X-ray analyses showed that highly-active catalysts were reduced only in traces before use. The ques is then immediately raised whether in that case the added copper is at al necessary to facilitate the reduction. In this connection the experiment we conducted on the basis of the X-ray investigations of Dr. Herbst will be found interesting. They show that the added copper performs a second function in the catalytic behavior that is at least just as important. As was discovered for the first time in the Ammonia Laboratory (Dr. Halle), when iron catalysts reduced at low temperature are employed a hexagonal iron carbide appears which, just as in the case of Hägg's iron carbide, probably has the formula Fe_2C on the basis of its structure and chemical analysis. However, this has hitherto not been described in the literature. This carbide is of particular interest because it has the same lattice structure as the analogous iron nitride Fe_2N and because it has very similar lattice dimensions. Thus, carbon, under the conditions of the hydrocarbon synthesis, can be placed into the iron lattic under certain circumstances just as nitrogen is placed nto the iron lattice in iron nitride formation. This "new, hexagonal carbide" seems to us to be a necessary, if not in itself sufficient pre-requisite, for especially good catalytic activity. Therefore, the information obtained by X-ray investigations (Dr. Herbst) to the effect that copper-containing iron catalysts are less sensitive to temperature and that this "new hexagonal" iron carbide in the presence of an addition of copper, which is always found in our catalysts, can stand a temperature around 100 degrees higher without into Hägg's carbide, is significant. The initial and barely noticeable conversion only begins to occur at 350 degrees with copper-containing catalysts and the conversion is completed at 450 degrees, whereas in the case of catalysts free of copper conversion begins to set in at 290 degrees and is complete at 330 degrees.

Let us now, after this discussion of problems of catalyst formation, return to our two catalyst combinations. In judging the respective advantages and disadvantages of the two catalysts we gave our preference to the c promoted with MgO because of the simplicity and ease of its productior The catalyst is rapidly precipitated. This is expediently accomplishe by running together the nitrate solution of the metals (Fe, Cu, Mg) ar alkali carbonate solution in a mixing nozzle (constant p_H). The finis precipitation mixture is collected in a receiver with the kieselgur su pended in H_2O or with the fine-pored silica gel, heated for a short ti (about 10 minutes) and then decanted. Since the precipitation quickly settles and the catalyst is readily washed, its preparation requires o a fraction of the time necessary for the preparation of the catalyst promoted with aluminum oxide. Catalyst efficiency is independent of tl manner and duration of drying.

The catalyst, in the form employed by us at the present time, has the following composition: Fe - Cu - MgO - K - kieselgur (or silic gel): 100 - 25 - 50 - 6/8 - 50. In unreduced form broken into pieces of 1-3 mm. it has a bulk weight of 0.4 - 0.45. The combination can und considerable variation within broad limits in regard to the proportions of magnesium oxide, potassium as well as kieselgur and silica gel witho revealing any basic change in catalyst efficiency. This is shown by th following table which contains a small selection of such precipitated catalysts (catalyst span velocity 240 liters gas/liter catalyst/hour, C H_2 = 1:2).

Catalyst number	for 100 Fe and 25 Cu		
	MgO	SiO_2	K

(Table on page 154)

Cat.	Synth.	CO	g.yield	% par.	% straight.-1)	g CH_4	Fraction 320-450	
nr.	temp.	consum.	/Ncbm	>320°C.	chain	/Ncbm	% olefins	% alcohol

(Table on page 155)

1) Determination of the degree of branching is accomplished by a purely empirical method worked out by Schaarschmidt with antimony pentachloride. This method was perfected by Dr. Leithe in the Ammonia Laboratory for use in transference to higher-boiling fractions and improved by Dr. Kotzschmar.

The catalyst was repeatedly tested in four-stage experiments in order to test its effectiveness on a somewhat larger scale. We will discuss these investigations in greater detail since the results seem quite remarkable.

Equipment: The small-scale laboratory experiments were conducted in pressure tubes of 15-16 mm. internal diameter situated in an electric furnace, but in the course of several years the tendency grew to embed these high pressure tubes in an oil bath in order to achieve a more uniform distribution of heat over the whole catalyst bed. The catalyst tube was then heated by the circulating oil which was pre-heated in an electric furnace. Temperature recording, which at first was undertaken by thermo-elements situated in the catalyst, was accomplished when using oil circulation by catalyst thermometers in the oil at the entrance and exit to the catalyst tube, after establishing the fact that a temperature loss of about 0.2 degrees occurred throughout the entire catalyst length in a 5 m. tube with equal oil and catalyst temperature.

The reactor system for the four-stage process consisted of 4 to 5 m. long iron catalyst tubes with an internal diameter of 16 mm. The contact zone was 4.50 m; the quantity of catalyst in the unreduced state amounted to 0.8-1.0 liters. Removal of the considerable amount c reaction heat was accomplished by oil circulation which was set up separately for each reactor. The high pressure gas lines were so arrar that in case of need each reactor could be removed from the series. If desired, the synthesis gas could pass to the next reactor without separation of the lighter boiling products. As usual a gas mixture obt by mixing the constituents in a $CO:H_2$ = 0.9-1:1 ratio served as synthes gas. It contained no carbon dioxide and only about 2 % N_2. The gas is largely free of sulfur, but to be certain, it was subjected to an addit purification in a copper preliminary reactor at 180 degrees and in 3 coupled towers with activated charcoal - caustic potash - activated cha Gas recording under pressure was accomplished by dry gas meters set in pressure-resistant chambers. In addition, a pressure flow manometer wa placed before the first reactor in order to note the constancy of flow. Separation of the solid and liquid products was accomplished after ever reactor:

Hot separator	120°	Paraffin - middle oil
Cold separator	20°	Middle oil - gasoline - water
Cooling by ice	0°	Gasoline - water
Low cooling	-70°	Gasoline - liquefied gas

Furthermore, it was possible to take gas analyses after every reactor. MgO catalysts produced in various ways served as catalysts. They were reduced in the furnace with H_2 at 220 degrees for 24 hours at a catalyst space velocity of 1000:1.

The following table summarizes the data obtained in three different experiments:

(Table on page 156)

The duration of the experiments differed greatly. Whilst two experiments ran for 124 and 141 days, the final experiment was interrupted after 42 days on account of trouble with the equipment.

The balance shows that the synthesis gas which was fed to the catalyst in a $CO:H_2 = 0.9-1:1$ ratio was converted in a 1.1-1.2:1 ratio.

The very remarkable yield of primary product, which is about a third higher than would otherwise be obtained in a reactor (1) under similar conditions of catalyst space velocity (120:1), can only be explained for the present by the varying high linear velocity of the gas with equal volume charge. This causes a better heat removal and dispersion throughout the entire catalyst area. The linear velocity of a catalyst tube of 16 mm internal diameter is per sec./12 at/227° C.:

in 1 tube of 5 m length	:	2.5 cm
in 4 tubes each 5 m	:	10.0 cm.

The last value lies at the border between the laminar and the turbulent flow area.

If the intermediate separation of the products which do not separate freely is omitted, then almost no important differences occur. The slight shifting in the boiling points of the higher boiling products to the extent to which it is real - only meets our desire to obtain long-chain products.

The following table contains several values for purposes of comparison.

(Table on page 157)

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(1) The data for the individual experiments in an individual 5 m catalyst tube are no longer available so comparative figures cannot be given.

<u>The influence of the Experiment Conditions</u>: Several of the influences felt in the preparation of the precipitated catalyst are mentioned here without in any way laying claim to exhaustiveness:

Method of preparation:	Selection of precipitating agent
	Concentration of precipitating solutions
	Temperature of the precipitation solutions
	P_H of the precipitation
	Speed of the precipitation
Promoter:	Time of addition
	Form of addition
	Formation of mixed crystal or compound
	Reciprocal influencing of several promoters
Carrier:	Purification
	Temperature pre-treatment
	Pore size
Alkalization:	Method of introduction of desired alkali co
Washing water:	Quantity and temperature
Drying:	Temperature
	Vacuum or gas current
	Sintering
	Bulk weight (pressed or broken up)
	Particle size
Reduction:	Temperature and time
	Gas space velocity
	Pre-treatment with foreign gases

These examples give an idea of the extraordinary abundance of variations possible in the preparation of the catalyst, even when its composition is known. Attention was directed to the special influences described above in the preparation of the MgO catalyst insofar as they were distinct and observed.

In addition to these problems arising in the preparation of catalysts, there is also the multiplicity of the experimental conditions which must be considered in evaluating the behavior of the catalyst which will be discussed here briefly. The difficulty in obtaining exact data is caused by the fact that several factors are always simultaneously at work so that it is often not at all practical to attribute this or that manifestation to a specific experimental condition.

Pressure: As is shown by the following examples selected from widely separated pressure stages, a pressure rise - with the same catalyst, equal catalyst space velocity and the same synthesis gas - acts in such a manner that, in order to achieve equal CO conversion, the temperature must be raised. At equal temperature and lesser pressure there is a better CO conversion. This can also be expressed in another way, viz., with equal temperature the lesser partial pressure of the ideal gas (1) ($CO:H_2$ in the synthesis gas in relation to the consumption in the synthesis) attains a better CO conversion.

(Table a on page 158)

In connection with the pressure rise there occurs a rise in gasification and, in general, a shortening of the hydrocarbon chains with decrease of olefins and an increase of alcohols. It remains uncertain to what extent the chain shortening is a function of the pressure for the

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(1) We are introducing the conception of the "partial pressure of the ideal gas" at this point because we will run across it again in another place.

temperature rise requisite for attaining the same CO conversion acts i the same direction.

Temperature: This is made clear by the following brief summary:

(Table b on page 159)

It can be seen from the table, furthermore, that the differe in the olefin and alcohol contents are very small in the same boiling ranges. Straightchainedness seems to drop with a rise in temperature. However, the values are not given since this is not at all certain.

Composition of the Synthesis Gas: A feed gas with a $CO:H_2$ ratio of 1: is more suitable for an iron catalyst, which directs the reaction towa the carbon dioxide side

$$3\ CO + 3\ H_2 = 2\ CH_2 + CO_2 + H_2O$$

than a gas rich in hydrogen, e.g., 1:2, which is used with the cotalt catalyst and is converted by it

$$CO + 2\ H_2 = CH_2 + H_2O$$

It remains uncertain whether the iron catalyst, too - severa indications point to it - acts toward the water side in the first stag the water gas process taking place only in the second stage. In any ca a hydrogen-rich gas contains too much hydrogen, which is available for hydrogenation, for the total reaction with the iron catalyst. Thus, a 1 : 2 gas contains only 66 per cent ideal gas for the iron catalyst in as the conversion gas goes to 1 : 1. It is therefore in accord with o previous working hypothesis if, under such experimental conditions the is preponderant in a metallic carbide:metal ratio, and if we find incr methane and liquefiable gas formation, more saturated products, and sh chained products with the same temperature and the same catalyst. This is confirmed by experiment. The richer the gas in hydrogen, the more marked the effect. Comparative experiments are still lacking.

(table c on page 160)

The Influence of the Synthesis Gas Ratio on the Experimental Results

Since a higher CO conversion is obtained (see the same findings under "pressure") at the same temperature with hydrogen-rich gas, whose ideal gas partial pressure is lower, an argument can also be put forward to the effect that the temperature for the catalyst is already so high under these synthesis gas conditons that the shortening of the hydrocarbon chains, as well as the increased methane formation, is conditioned by it. We are inclined toward the first viewpoint.

The influence of higher inert gas contents has not been investigated. Since we are dealing here also with a reduction in ideal gas partial pressure, we should expect behavior as in hydrogen-rich gases, i.e., a shortening of the hydrocarbon chains and a better CO conversion at the same temperature than with a gas free of inert gas.

The problem of time contact, i.e., of catalyst space velocity per unit of time, is the last point of the external experimental conditions to be mentioned. This effect is made clear by the following table:

(Table on page 161)

A smaller CO conversion is obtained with the same temperature and a shorter contact time, a maximum of long-chain products being formed with space velocities of 720:1 and 960:1, whilst substantial differences between olefin and alcohol content are not pronounced. When the CO conversion i the same, for which the temperature must be increased with a higher vol space velocity, the olefin and alcohol content remain almost the same ir equal boiling fractions, while the chain length sometimes increases and sometimes decreases. In this connection there are various contradictor experimental results.

(Table e on page 162)

These discrepancies, as well as the above-mentioned maximum formation, may be explained by the more equalized heat relations in the case of a higher linear velocity of the gas (Cf. comments on the four-stage process).

In concluding these researches on paraffin recovery with iron precipitated catalysts, it should be mentioned for the sake of thoroughn that we had advanced so far toward the end of the war that we were able run a 600 liter experimental reactor filled with MgO catalyst which was produced batchwise, formed on a grooved cylinder (designed by Dipl. Ing. Misenta) and dried beforehand. Frequent troubles with the synthesis apparatus prevented the catalyst from coming to full production. Three a half tons of paraffin recovered during a period of temporary uninterru operation were lost by fire during paraffin oxidation in an air raid. A a result of the effects of the air raid, which also precluded resumption of plant operation, a new catalyst installation was not tried again, alt the apparatus had been perfected to such a point toward the end of the o and only experiment that it ran uninterruptedly and gave good balances. primary product obtained with unsatisfactory CO conversion contains 63 pe cent of snow-white paraffin with a boiling point in excess of 320 degree

Investigations on the Recovery of Olefins

The recovery of a primary product which would be rich in olefins in all boiling ranges is presented by the prospect of advantageously using certain fractions where saturated products can not be employed to any great extent, i.e., the middle oil fraction (B.p. 195-320 degrees) for the Oxo reaction or sulfonation if products of this boiling range are considered for working up to detergents. In this connection the possibility would always remain of purposefully converting the olefins of the higher-boiling fractions into saturated hydrocarbons by a simple hydrogenation. It is therefore perfectly comprehensible if, along with the researches on paraffin recovery, the problem of olefin and alcohol recovery is again and again put into the forefront.

Olefins (1) and alcohols are now produced in noteworthy quantities with the above-mentioned iron precipitated catalysts, working with CO-rich gases. Even more favorable results were obtained with fused catalysts even though here too conversions to saturated products occurred depending on composition.

The use of such fused catalysts, produced by the oxidizing-melting of iron in the presence of promoters in an oxygen current after the manner of the ammonia catalyst, occurred to us. They represent an excellent material because of the speed with which they can be produced and the ease and the exactness with which they can be reproduced.

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(1) Determination of the olefin content was accomplished by the iodine numbers which were determined by the bromine method of Kaufmann. This method always gave corresponding values as compared with those of the hydrogenation method with platinum catalysts and those of the method of Dr. Klein, Oppau, in which the addition of bromine to the double bond occurred with low temperature cooling in order to prevent a substitution.

It would be going too far afield to cite all the experiments directed toward the recognition of favorable combinations of catalysts. The investigations did not merely confine themselves to the modification of the ammonia catalyst by replacing the aluminum oxide by other oxides, such as MgO, CaO, BeO, etc. which were unreducible under the reduction and experiment conditions, but also studied the influence of additions of metallic oxides which are reducible like the iron, the actual catalyst metal: copper, silver, nickel and cobalt.

The result of these experiments was that thenceforth we turned for the most part to fused catalysts containing magnesium oxide and alkali as promoters. Relinquichment of aluminum oxide as promoter was caused by the observation that with it smaller total outputs with less straight-chain hydrocarbon chains were obtained.

In investigating the iron-magnesium oxide-potassium-fused catalysts we had to consider two limiting cases.

1. Catalysts in which the MgO content was 0, that is, which only contained iron and alkali, and
2. Catalysts in which the alkali content was 0, that is, which contained no further addition apart from MgO.

1\. The catalyst free of MgO yielded products with the highest olefin value This may very well be explained by the high reaction temperature of 320 - 3 degrees requisite because of the failure of other promoters. It is notewor that no soot formation occurred despite this stated high temperature.

2\. The catalyst free of alkali yielded a small amount of olefins, about 20 per cent(1), and only few products boiling over 320 degrees

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(1) The values for olefins cited in the text always refer to the 320-450 degrees paraffin fraction.

the amount of which can be improved by increased additions of MgO. With these catalysts we soon approached the products of the paraffin-producing precipitated catalysts. This became especially marked when we turned to introducing acid additions into the catalysts. Products containing only up to 10 per cent of olefins are obtained by melting in SiO_2. The proportion of the total yield boiling above 320 degrees, however, was slight, and the 70 per cent straightchainedness of the obtained product left too much to be desired for this type of catalyst to be used in our investigations directed toward the production of paraffin.

The two limiting cases show the markedly reaction-directing influence of the alkali addition toward olefin production. Even a slight proportion of alkali in the iron-magnesium oxide mixture causes a speedy rise of the olefin content in the primary product, as well as an increase in the chain length. This rise in olefin content, however, does not increase linearly with the alkali content but, starting with a catalyst free of alkali which produces 20 per cent olefins, rapidly attains an end value of about 75 per cent olefins. This is a value that can hardly be outstripped even with higher alkali contents.

It is noteworthy that the modification of product quality in the above described manner is not dependent on the absolute alkali or magnesium content (i.e., dependent on the actual catalyst metal iron); the MgO:K ratio is decisive.

This result was confirmed by a series of further experiments with higher MgO contents and also correspondingly higher alkali contents. As long as the ratio was kept the same the same products were always obtained.

In summary we give the result of several series of experiments:

Experiment Series with Iron-Magnesium Oxide-Alkali

Catalyst space velocity 480:1; synthesis gas: 33 % CO

Cat. Comp. Fe MgO K %	Synth. temp.	CO convers.	gram yield /Nm^3	% Par. 320°	Straight chain	Par. % olef.	frac. % alc.

In all the above catalysts used Hägg's carbide Fe_2C was shown X-rays to be present.

If the alkali in the iron-magnesium oxide-fused catalyst is replaced by an acid constituent (SiO_2)

(Tables on page 163)

Cat.Comp. %FE %MgO %SiO	Synth. temp.	CO convers.	g.yield /Nm^3	% Par. >320°	% Straight-chain	Paraffin % olef.	fract % alc

the olefin content will drop somewhat to rise again with greater SiO_2 additions, producing the following graph:

Dependence of the Olefin Yield on the Acid and Alkali Content with the Iron-Magnesia-Fused Catalyst

(Graph on page 164)

After the synthesis X-rays show magnetite (Fe_3O_4) along with Hägg's carbide to be mainly recognizable in these alkali-free fused cata

Roughly the same behavior can be established in regard to olef content if, instead of completely leaving out the alkali in the MgO fuse catalyst, its quantity is kept constant while the quantity of silicic ac is increased.

Cat. Comp. %MgO %K %SiO_2	Synth. temp.	CO convers.	g.yield /Nm^3	% Par. >320°	% straight-chain.	Paraffin % olef.	fract % alc

(Table at bottom of page 164)

Similar behavior can be expected with such fused catalysts where the quantity of silicic acid was kept constant and the quantity of alkali was varied. As can be seen from the following table, however, the differences in the olefin content of the soft paraffin fraction are not very considerable even though a slight rise in the expected direction occurred with an increasing amount of alkali. A synthesis gas containing 50 per cent of CO as compared with 33 per cent in the previous experiments was used in this new series of experiments; the catalyst space velocity was 240:1 instead of 480:1.

(Table on page 165)

The X-ray findings bear notice. The catalyzing substance alters with the increasing alkali content. Whereas magnetite predominated at the start, more and more Hägg carbide appears along with the magnetite until finally, at the point where only Hägg carbide was expected, the new hexagonal carbide made its appearance.

In summary, we can say on the basis of the olefin values cited in the preceding tables that the only catalyst of importance for the recovery of unsaturated hydrocarbons(1) is the fused catalyst, without

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(1) The olefins obtained with the fused catalysts were produced on a somewhat larger laboratory scale and subjected to several tests. They were sulfonated and the products thus obtained tested as detergents. Their detergent properties almost approach those products obtained from cracked olefins and even surpass them in latherine power. They were also subjected to the Oxo reaction and here, too, lived up to all requirements.

The lower gasoline fractions were checked by the motor test. The following octane numbers were obtained:

	Unleaded	Leaded (1cc/1 liter)
M. oct. no.	54.5	-
R. oct. no.	52.5	86.5

addition of silicic acid, promoted with MgO and alkali and composed of Fe - MgO - K = 100 : 5 : 2.5. The catalyst is reduced at about 500 degre in about 48 hours with an hourly catalyst space velocity of 2000:1. This is not to say that a thorough reduction is necessary. Our investigations showed that catalysts with a degree of reduction of 30 - 100 per cent give practically equal yields of products of very similar composition(1). A reduction of the synthesis temperature with fused catalysts - as in the case of precipitated catalysts - is attained by catalyst formation by mean of a higher linear flow velocity of the reducing gas. Nevertheless temperatures of 225-245 degrees are still necessary when synthesis gas is used with a space velocity of 200:1.

In this last respect the behavior of Al_2O_3-containing fused catalysts is more favorable. Their synthesis temperature is again lower by 10-20 degrees. The olefin content of the primary product, however, was substantially lower(1) than the olefin content attained with the MgO fused catalyst. In this respect it departed from the series of the olefin-produc catalysts.

Just as the addition of Al_2O_3 lowers the synthesis temperature, in like manner other additions to the fused catalysts act in other directio In this connection the action of fluoride additions in the form of CaF_2(2), Al F_3, FeF_3(2) were of interest. The former largely direct the synthesis toward low-boiling products at a low synthesis temperature, the other two, however, are rather characterized by the fact that they direct the synthesis toward the formation of low-boiling products at temperatures of 170-200 degr

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(1) The recorded data are no longer available so that the series cannot be checked with figures.

(2) A CaF_2-containing fused catalyst was also used in the comparative exper ments of the iron catalysts of various firms, at the Schwarzheide, Ruhl plants be the Ammonia Laboratory and was proved to be reliable (autumn

however - and this is of scientific interest - in the case of these low temperatures, i.e., with slight CO conversion, only water appears as a side product and not carbon dioxide, as is usual with iron catalysts. The latter only begins to appear increasingly with a rise in the CO conversion, i.e., at higher temperatures.

Alcohols:

We can summarize very briefly the experiments conducted by us for the production of a primary product containing a substantial content of alcohols(1) since the results achieved up to now are quite unsatisfactory. Even when a higher percentage of alcohols occasionally appeared in one or another fraction, the fraction as such was so small that the gram yield of alcohols was of practically no importance as compared with other products.

The first experiments disclosed that rather large amounts of alcohols were formed especially at the start, i.e., at low temperatures; furthermore, that alcohol formation was promoted by a rise in pressure. Therefore precipitated catalysts as well as fused and roasted catalysts were tested at high and medium pressure. With none of these types did we achieve our hoped for aim of substantially improving the quantity of alcohol in grams/Ncbm. We strove to attain a catalyst which we could use at a low temperature since this was connected with a decrease in methane formation and an increase in total output as well as the formation of higher alcohols. The latter is obtained on the level of previous investigations in particular with fused and precipitated catalysts, the former

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(1) The most basic investigations in this field were conducted by Leuna but we do not possess any data on the results.

being superior to the precipitated catalysts. The roasted catalysts are especially suitable for the synthesis of lower alcohols up to C_4; at lower temperatures, (slight consumption of CO) however, higher alcohols, which are of importance as starting materials for detergents, are formed up to 25 per cent of the total product.

Dr. A. Scheuermann

In addition to the author, the following persons participated for varying periods of time in the researches of the Ammonia Laboratory on hydrocarbon synthesis from carbon monoxide and hydrogen at atmospheric and medium pressure:

- Dr. Bartholome
- Dr. Döll
- Dr. Kärtkemeyer
- Dr. Kotzschmar
- Dr. Marecek
- Dr. Meisenheimer
- Dr. Schmole
- Dr. Vorbach

Table (1) (referenced on page 58)

233	1096a	190	71	1,0	6,5	0,8	139	61	100
269	1136	189	71	0	8,0	0,2	135	67	97
275	1138	182	67	0,6	5,6	0,4	130	60	97
297	1133	188	73	1,2	8,8	0,1	137	61	99
673	1444	180	75	1,0	9,5	0,1	133	58	95
Als Mittelwerte ergeben sich:							= 0,324	kg/Ltr.	Kt/Tag
		186°	71	1,0	7,7		135	61	98

Table (2) (referenced on page 58)

Die Verteilung des Primärproduktes auf die Siedebereiche

Vers.Nr.	-195	- 320	- 450	>450
233	16,6	22,1	23,9	37,4
269	15,3	17,4	26,0	40,3
275	19,5	20,2	26,2	33,9
297	18,7	18,5	24,7	36,6
673	17,9	28,4	24,4	28,8
Mittelwerte:	18 %	21 %	25 %	36 %

TABLE (referenced on top of page 59)

Vers.Nr.	Kont.Nr.	Temp.	CO-Verbr.	im Abgas $\%CO_2$	im Abgas $\%CH_4$	$\%K_2O$ im Kont. 100 Co	g Ausbeute feste + fl. Prod./Ncbm.
233	1096a	181	51	0	3,2	0,8	95
275	1138	174	42	0,2	2,8	0,4	86
297	1133	177	50	0,4	3,2	0,1	98
673	1444	160	55	0	3,1	0,1	77
Mittelwerte:		173	50		3,1		89

TABLE (referenced middle of page 59)

Vers. Nr.	Kont. Nr.	Gehalt $\%K_2O$	Gehalt $\%Co$	Temp.	CO-Verbr.	im Abgas $\%CO_2$	im Abgas $\%CH_4$	g Ausb. feste + flüss.Pr. /Ncbm	% Par. >320°	%Geradkettigk.
325	1193	0,1	40,2	188	69	1,2	6,4	121	72	94
298	1132	0,1	37,6	177	79	0,8	12,1	135	67	100
297	1133	0,1	30,0	188	73	1,2	8,8	137	61	99
303	1134	0,1	25,1	182	74	0,5	8,9	236	62	100
299	1135	0,2	20,8	180	76	3,4	9,0	136	58	98

TABLE (referenced on bottom of page 59)

	- 195	- 320	- 450	>450
Vers.Nr.325	12,8	13,9	19,7	52,7
298	17,1	14,2	21,0	46,2
297	18,7	18,5	24,7	36,6
303	18,4	18,8	26,6	35,6
299	21,9	19,7	24,1	33,7

TABLE (referenced top of page 60)

Vers. Nr.	Kont. Nr.	%K_2O/ Kont.	Temp.	CO Verbr.	im Abgas %CO_2	%CH_4	g Ausb. feste + flüss.Pr. /Ncbm	%Par. >320°	% Geradkettigk.
275	1138	0,4	182	67	0,6	5,6	130	60	97
233	1096a	0,8	190	71	1,0	6,5	139	61	100
234	1096c	1,3	209	69	2,0	7,4	127	54	99
247	1096d	2,4	223	73	6,3	9,1	104	39	98

TABLE (referenced middle of page 60)

275		174	42	0,2	2,8	86
233		181	51	0	3,2	95
234	s.oben	198	49	0,6	3,3	77
247	see above	200	58	1,8	4,5	72

TABLE (referenced middle of page 60)

ers. r.	Cat. no. Kont. Nr.	% in catalyst 1. Kont. $\%K_2O$	% Co.	Temp.	CO Verbr. consumption	in off gas im Abgas $\%CO_2$	$\%CH_4$	yield g Ausb. /Nobm	% Par. >320°	% Geradkettigk. Straight	Kühlung Cooling olefins % Olefine 195–250	250–320	320–450°	alcohols % Alkohole 195–250	250–320	320–450°	% Kontr.
				Synthesegas 1 : 1 Synthesis gas		5 Liter-Ofen Heißwasser - reactor hot water											
83	1470	0,2	32,3	170	38	0	1,1	71	49	85	29	19	17	27	21	17	47
				175	49	0	2,5	96	58	84	33	19	14	29	23	17	56
Red.:5^h/350°/1000:1				195	62	1,8	3,1	115	54	88	38	23	16	19	8	8	62
				Synthesegas 1 : 2		Oelumlaufheizung oil circulation heating											
73	—	0,2	32,3	160	50	0	2,7	97	53	95	12	9	9	15	-	25	55
				170	56	0	1,4	93	69	-	10	6	3	10	9	5	-
Red.:5^h/350°/1000:1				180	71	1,0	9,4	138	58	95	10	3	3	8	3	3	72

TABLE (referenced bottom of page 60)

Vers.673:	9.-13. Tag	160°	3,5 % CH_4
	14.-19.	160°	2,7 "
	20.-26.	160°	2,2 "
	27.-34.	160°	1,8 "

TABLE (referenced on page 66)

	mit Al_2O_3 aktiv. Kontakt Catalyst promoted with Al_2O_3	mit MgO aktiv. Kontakt Catalyst promoted with MgO
Kontaktbelastung in Vol Gas/ 1 Vol Kont./Stunde Space velocity in vol. gas/1 vol. cat./hour	240 : 1	240 : 1
CO-Umsatz Co conversion	80	70
Reaktionstemperatur reaction temperature	210	235
Ges.Ausbeute in g/Ncbm bei einmaligem Durchsatz Total yield in grams/Ncbm with single ~~[illegible]~~ operation	82	90
Siedefraktionen: Boiling fractions		
-195°	23	40
195° -320°	18	15
320° -450°	24	20
>450°	35	25
% Geradkettigkeit des Paraffins Straightchainedness of the paraffin	91	81
% Olefine in d.Paraffinfraktion olefins in the par. fract.	8	8
% Alkohole in d.Paraffinfraktion alcohols in the " "	6	3

TABLE (referenced on page 68)

Gas	Reduktion		Dauer	Synth. temp.	CO-Verbr.	g feste + flüss.Prod.	% Par. >320	g CH_4/Ncbm
	Temp.	Belastung						
H_2	300°	400:1	15h	238	75	73	39	24
ohne Reduktion			-	240	77	97	53	14
H_2	180°/220	5000:1	15-20	222	64	88	60	14
Synth.gas	200°/250°	5000:1	"	214	62	82	60	16

TABLE (referenced bottom of page 70)

Kontakt Nr.	auf 100 Fe + 25 Cu		
	MgO	SiO_2	K
1188	36	50	6
1178	48	48	6
1218	42	49	11
1220	47	95	12
1238	34	88	10
1235	32	91	7
1205	89	49	8
1204	95	48	8

TABLE (referenced top of page 71)

Kont. Nr.	Synth. Temp.	CO-Verbr.	g Ausb./Ncbm	% Par. >320	%Gerad.- 1) kettigk.	g CH_4 /Ncbm	Fraktion %Olefine	320-450 % Alkoh.
1188	210	53	86	70	95	14	23	5
1178	210	46	67	57	85	12	28	2
1218	222	71	88	52	94	21	14	4
1220	210	50	72	76	92	14	6	2
1238	225	52	78	78	88	—	22	4
1235	215	56	75	54	84	—	19	5
1205	218	63	91	54	93	14	13	3
1204	230	66	99	70	86	12	25	7

TABLE (referenced on page 73)

Vers.Nr. Expt. no.	521/524		587/590		
Kont.Nr. Cat no.	1263		1382		
Synthesegas $CO:H_2$ = Synthesis gas	1 : 1		1 : 1		
Kontaktbelastung catalyst space velocity 1 Gas/1 Kt/Stunde	240 : 1		120 : 1		
Zwischenabscheidung intermediate separation	mit with Tiefkühlung low cooling	ohne without	mit Tiefkühlung		ohne
Synthesetemperatur °C synthesis temperature	240,235,230,225		230		230
Ausbeute g/Ncbm yield	76	76	119	120	100
Tag der Laufzeit running time in days	119.	122.	19.	32.	33.
Kontraktion % contraction	46	37	46	43	43
CO - Umsatz % conversion	59	51	68	68	65
CO - Umsatz zu % CO_2 conversion to % CH_4 % feste + fl.KW solid + liquid	25 5 29	22 4 25	29 2 37	27 2 39	29 3 33
boiling situation of solid + liquid Siedelage d.festen + fl. Produkte products : Benzin gasoline -195	19,3	9,8	14,2	12,5	15,1
Mittelöl middle oil -250	13,7	18,5	9,8	5,2	3,4
-320	9,9	11,4	7,8	8,6	9,5
Paraffin -450	20,5	31,2	22,3	22,9	19,2
Hartparaffin hard paraffin >450	35,3	37,6	44,7	50,5	51,7
	98,7	98,5	98,8	99,7	98,9

TABLE (referenced on bottom of page 73)

Vers.Nr. Exp. Nr.	587/590	620/623	677/680
Kont.Nr. Catalyst nr	1382	1383	1462
Kontakt-Analyse: Catalyst analysis Fe	23,6	24,2	23,4
Cu	5,6	6,2	6,2
MgO	2,1	7,4	8,3
SiO_2	33,7	23,3	22,2
K	2,4	2,5	3,0
CO_2	2,2	6,0	6,0
Synthesegas: Synthesis gas CO : H_2 =	0,9 - 1 : 1		
Kontaktbelastung- 1 Gas/1 Kont./St. catalyst space velocity	120 : 1		
Synthesetemperatur: Synthesis temperature	240°C	230°C	225°C
g Primärprodukt + Gasol/Nobm grams primary product	147	145	142
Raumzeitausbeute space-time yield kg Prod./Liter Kontakt/Tag catalyst / day	0,42	0,42	0,41
Kontraktion % contraction	53	57	51
CO - Umsatz % conversion	83	83	70
% CO - Umsatz zu conversion to CO_2	33	32	25
CH_4	3	4	2
higher höhere KW	47	47	43
total insgesamt:	83	83	70
Siedelage: Benzin - 195° boiling situation of solid + middle oil the liquid paraffin products	19%	24%	21%
d.festen + Mittelöl-320°	15	23	18
flüssigen Paraffin >320°	66	53	61
Produkte	100	100	100
Mittelölfraktion 195 - 250° middle oil fraction % Olefine olefines	63	53	48
% Alkohole alcoholes	18	16	13
% Geradkettigk. straight chainedness	48	42	52
Mittelölfraktion 250 - 320° middle oil fraction % Olefine	52	42	47
% Alkohole	16	14	12
% Geradkettigk.	64	68	70
Paraffinfraktion 320 - 450 % Olefine	35	28	34
% Alkohole	8	9	10
% Geradkettigk.	80	77	83

TABLE A (referenced on page 75)

Tabelle a

Vers.Nr. Expt. no.		419	418	450	476
Kontakt Nr. Cat. no.		1251	1251	1263	1263
Druck pressure		12	200 at	12 at	50 at
$CO:H_2$		1:1	1:1	1:1	1:1
Kontakt-Belastung catalyst space velocity		240:1	240:1	240:1	240:1
Synthese-Temp. synthesis temp		215	265	215	225
CO-Umsatz CO conversion		32	31	29	30
g Ausbeute/Nm^3 an festen u.flüss.Prod. gram yield per m^3 of solid and liq products		61	52	56	48
g C_1-C_5/Nm^3		4	11	3	12
Produkt- prod. zusammen- comp. setzung in ~ %	-195	7	34	17	41
	-320	7	17	12	28
	-450	14	19	21	17
	>450	72	30	50	12
% Olefine	195/250	-	44	48	23
	250/320	-	39	48	20
	320/450	41	44	36	18
% Alkohole	195/250	-	23	16	57
	-320	-	32	18	57
	-450	13	42	27	43

TABLE B (referenced on page 76)

Tabelle b

Vers.Nr. Expt no			444			
Kontakt-Nr. cat. no			1251			
CO : H_2			1:1			
Kontakt-Belastung space velocity			720:1			
Synth.Temp.		215	235	245	255	275
CO-Umsatz co conversion		18	31	44	54	72
g Ausbeute an festem u. flüss.Prod./Nm^3 gr. yield		36	59	72	78	84
g C_1-C_5/Nm^3 [illegible] and olefines		0,7	4,2	17,7	32	63
Produkt- prod	-195	7	19	25	34	37
Zusammen- comp	-320	6	13	15	19	36
setzung in ~	-450	17	20	21	19	16
%	>450	70	48	39	28	17
% Olefine	195/250	-	54	54	56	61
	-320	49	49	46	46	43
	-450	34	37	35	32	33
% Alkohole	195/250	-	-	6	5	-
	-320	11	-	14	4	-
	-450	15	12	8	3	-

TABLE C (referenced on page 77)

Tabelle c

Über den Einfluß des Synthesegas-Verhältnisses auf die Versuchsergebnisse.

Vers.Nr. Expt no.		511	508	499	529
Kont.Nr. cat. no		1263	=	=	=
% CO		50%	33	50	33
Kont.Belastg. space velocity		240:1	=	720:1	=
Synth.Temp.		240	245	250	250
CO-Umsatz Co conversion		46	72	33	60
g Ausbeute/Nm^3 gr. yield		80	75	55	45
g C_1-C_5 /Nm^3		14	24	12	37
Produkt- prod	-195	18	23	9	43
zusammen- comp.	-320	20	24	19	29
setzung	-450	18	25	21	17
%	>450	42	26	50	11
% Olefine	195/250	50	24	58	42
	-320	44	16	43	29
	-450	22	8	29	14
% Alkohole	195/250	27	9	9	4
	-320	27	6	6	1
	-450	10	9	3	1
Geradkett.		80	91	76	-

TABLE D (referenced on page 77)

Tabelle d

table headings same as before

Vers.Nr.		511	533	499	538	516
Kontakt Nr.		1263				
CO : H_2		1:1	1:1	1:1	1:1	1:1
Kontakt-Belastg.		240:1	480:1	720:1	960	2400:1
Synth.Temp.		240	240	240	240	240
CO-Umsatz		46	34	24	23	11
g Ausbeute/Nm^3 an festem u.flüss. Produkt		80	61	43	41	12
g C_1-C_5/Nm		14	8	6	6	10
Produkt-zusammen-setzung %	-195	18	17	9	5	21
	-320	20	21	20	19	20
	-450	18	23	21	21	24
	>450	44	39	50	55	35
% Olefine	-250	50	51	57	57	54
	-320	44	42	42	49	46
	-450	32	25	30	33	37
% Alkohole	-250	27	29	19	23	30
	-320	27	23	16	22	30
	-450	10	13	8	15	19

TABLE E (referenced on page 78)

Tabelle e.

Vers.Nr.		536	529	411	406	444	432
Kontakt-Nr.		1263	-	1238	-	1251	-
CO : H_2		1:2	1:2	1:2	1:2	1:1	1:1
Kontakt-Belastung		240:1	720:1	240	480	120:1	240:1
Synth.Temp.		230	250	225	235	215	220
CO-Umsatz		64	60	65	63	39	39
g Ausbeute/Nm^3 an festem u.flüss. Produkt		70	45	81	74	59	69
g C_1-C_5/Nm^3		18	37	8	13	70	10
Produkt-zusammensetzung	-195	22	43	15	18	25	8
	-320	23	29	26	16	15	11
	-450	23	17	17	22	21	15
	>450	32	11	42	44	39	66
% Olefine	-250	33	42	-	-	54	53
	-320	22	29	-	-	50	47
	-450	12	14	22	20	36	38
% Alkohole	-250	22	4	-	-	-	18
	-320	14	1	-	-	6	9
	-450	5	1	4	10	5	15

TABLES (referenced on page 82)

Kont.Zusammensetzung %Fe	%MgO	% K	Synth.temp.	CO-Umsatz	g Ausbeute /Nm³	%Par. >320°	%Geradkettigk.	Paraffin frakt. %Olef.	%Alkohol	Schüttgewicht
70,2	3,4	0	253	80	70	24	65	19	4	2,94
70,4	3,5	0,26	245	83	89	62	68	47	-	2,86
69,9	3,5	0,44	240	82	89	69	68	59	-	2,70
69,9	3,3	0,61	252	80	74	73	74	66	29	2,83
68,4	3,2	1,21	245	78	78	59	66	68	18	2,77
68,0	3,3	1,90	253	75	62	50	76	77	23	2,75
67,0	3,2	1,94	255	90	108	48	74	73	23	2,51
63,3	3,0	5,05	283	80	77	49	62	79	10	2,38

Kont.Züsammensetzung % Fe	%MgO	%SiO₂	Synth. temp.	CO Umsatz	g Ausb. /Nm³	% Par. >320	% Geradkettigk.	Paraffinfrakt. % Olef.	%Alkoh.
70,2	3,4	--	253	80	70	24	65	19	4
69,8	3,3	0,85	268	70	41	13	66	7	3
69,5	3,4	1,63	277	73	52	12	70	27	1
68,2	3,3	3,15	263	78	55	39	78	36	5

GRAPH (referenced on page 82)

Abhängigkeit der Olefin-Ausbeute vom Säure-und Alkaligehalt bei Eisen-Magnesia-Schmelzkontakt

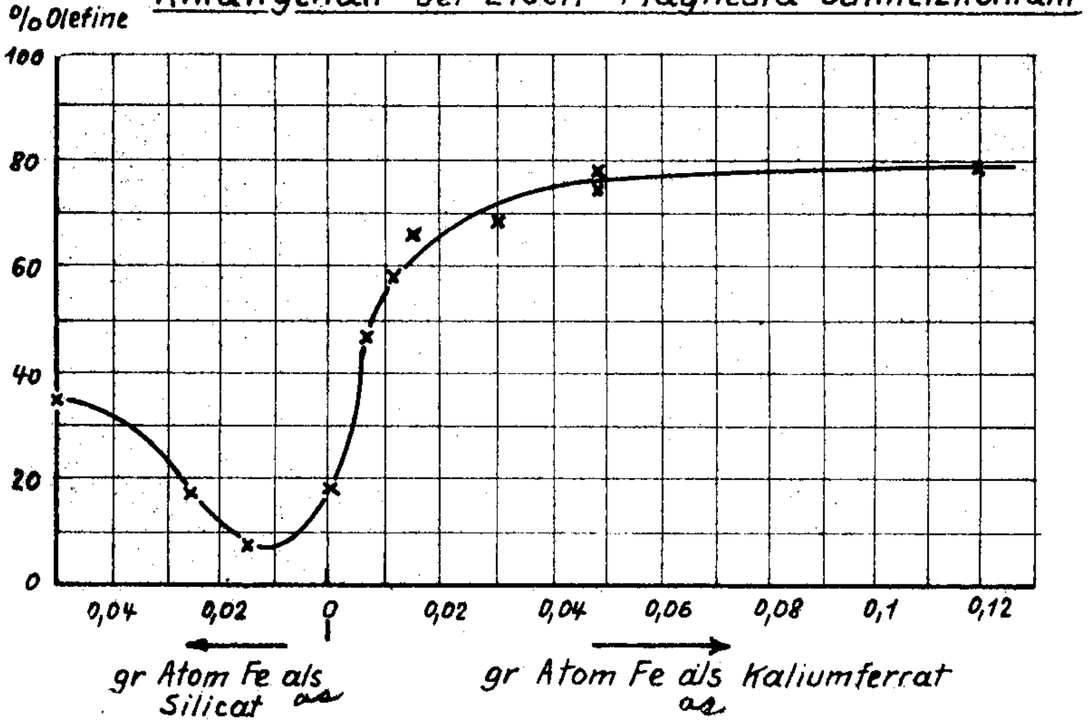

TABLE (referenced top of page 83)

Kontaktzusammensetzung %Fe	%MgO	% K	%SiO$_2$	Synth. temp.	CO-Umsatz	g Ausb. /Nm^3	% Par. > 320°	Gerad-kettigk.	Paraffin frakt. %Olef.	%Alkoh.
70,9	3,0	0,24	--	239	86	77	47	83	40	16
69,5	3,4	0,31	0,82	244	75	79	34	73	21	5
69,5	3,0	0,22	1,48	248	89	71	16	65	8	0
68,4	3,3	0,20	2,72	243	80	76	27	72	35	34

Zusammensetzung composition				Synth.	CO-	g Ausb. yield	% Par.	% Olefingehalt content			% Alkoh.	-gehalt content		Röntgenbefund
Fe	MgO	K	SiO$_2$	temp.	Umsatz conversion	m^3	>320	-250	-320	-450	-250	-320	-450	x-ray findings
70,5	2,6	—	—	230	48	87	29	67	52	34	10	4	2	Fe, Fe$_3$O$_4$
70,7	3,1	—	1,76	230	33	58	25	53	41	28	7	3	5	Fe$_3$O$_4$, Fe$_2$C Hägg
69,0	2,7	0,15	1,80	230	61	93	41	65	50	34	23	13	5	little wenig Fe$_3$O$_4$, FeC Hägg
68,2	3,3	0,50	1,86	230	77	118	38	70	55	40	22	9	5	trace of Spur Fe$_3$O$_4$, Fe$_2$C Hägg
68,0	3,2	1,28	1,94	230	72	122	47	65	55	43	29	24	12	n.h.Carbid, some etwas Fe$_2$C Hägg