

Synthesis with Iron Catalysts

By the end of the war the research and development work on iron catalysts had reached such a stage that Ruhrchemie were making plans for full-scale tests before introducing them as standard catalysts for medium pressure synthesis. Lurgi now consider that, as a result of smaller scale tests, they would be prepared to build a plant and give a guarantee of 150 g. liquid and solid products/N.c.u.m.. Dr. Michael, of I.G. Farben, pointed out, however, that on account of the ease with which iron catalysts bolt, the step up from the semi-technical scale to full-scale might not be quite a straightforward one.

Unlike the case of synthesis with cobalt catalysts, where most of the work has centred round one standard catalyst, a large number of iron catalysts have been developed, which require very different conditions for synthesis and give different types of products. The preparation and performance of the more important of these catalysts will be given in some detail in this section, but before this is done a few more general points, which apply to most iron catalysts, will be considered.

Catalyst Costs.

In comparing costs for iron and cobalt catalysts, it must be remembered that the cobalt required to make up for losses is not included in the cost data given by Ruhrchemie. If therefore the steps in the preparation are about equally costly, it is a question of comparing the cost of the cobalt loss with the cost of the extra chemicals needed in the preparation of iron catalysts because the cost of the iron, the raw material, is small. Ruhrchemie consider that it is quite possible for these extra chemicals to outweigh the cobalt loss factor and so to make iron catalysts the more

expensive. They gave the following estimate, Table 43, for the manufacture of an Fe 100: Ca 10: Cu 5: kieselguhr 50 catalyst, based on small-scale discontinuous working. The calculation is for a scale of working to produce 70 reactor charges per month, each of 10 cu.m., and assumes that the used catalyst is worked up as completely as possible, so that additions of iron, copper and calcium are only required to make up for losses. No credit is allowed for recovered sodium nitrate.

Table 43.

Estimated Costs for an Iron Catalyst, Ruhrchemie

	Quantities per kg. Fe	Costs, RM per kg. Fe
Wages		0.57
Salaries		<u>0.10</u>
		0.67
<u>Energy</u>		
Electric Power	7.0 kwh.	0.18
Steam	105.0 kg.	0.45
Fresh Water	0.45 cu.m.	0.04
Heating Gas	2.0 cu.m.	<u>0.05</u>
		0.72
<u>Materials</u>		
Soda Ash	4.78 kg.	0.39
Nitric Acid	2.0 kg.	1.20
Condensate Water	0.2 cu.m.	0.28
Gas for pretreatment	6.5 cu.m.	0.38
Nitrogen	1.0 cu.m.	0.03
Carbon dioxide	0.9 kg.	0.10
Potassium hydroxide	0.06 kg.	0.03
Steel	0.10 kg.	0.02
Copper	0.005 kg.	0.01
Lime	0.03 kg.	0.01
Kieselguhr	0.58 kg.	0.10
Filter Materials		0.1
Repairs and Maintenance		0.6
Auxiliary Plant and Other Costs		0.3
Laboratory Costs		<u>0.3</u>
Total Costs		<u>5.24</u>

Pretreatment.

Just as cobalt catalysts require reduction in hydrogen before they become active for synthesis, so iron catalysts require pretreatment with water-gas, synthesis gas, carbon monoxide or hydrogen at atmospheric pressure or at reduced pressures before they can be used for synthesis at medium pressures. Ruhrchemie could give no general conclusions on the relative merits of the various methods that have been proposed for carrying out the pretreatment, and they thought that possibly different types of catalyst required different pretreatments. They gave the following rather tentative scheme:-

- (1) Pretreatment with hydrogen.
 - a) Normal reduction. Maximum temperature 300°C ., time 30 - 60 mins., gas rate 6,000 litres/litre catalyst/h., using 75% H_2 , 25% N_2 . This gives good results. For wax-forming catalysts very mild treatment is required.
 - b) Longer time and higher temperature. $T = 325 - 400^{\circ}\text{C}$., time 24 hours, gas rate as before, is a good pretreatment for very concentrated catalysts.
 - c) Low gas rate and low temperature. This gives poor results.
 - d) High gas rate and low temperature. The first results were good but researches have not been completed.
- (2) Pretreatment with hydrogen, followed by carbon monoxide or water-gas. It is the initial hydrogen treatment that determines the activity of the catalyst, the subsequent carbon monoxide or water-gas treatment has little effect.
- (3) Pretreatment with carbon monoxide. $T = 250 - 325^{\circ}\text{C}$., time 24 hours, using pure CO or CO largely diluted with nitrogen. Atmospheric pressure. In nearly all cases this gives good results.
- (4) Pretreatment with water-gas. Using gas with 39% CO, 48% H_2 at $250 - 300^{\circ}\text{C}$. and gas rates from 200 - 6,000 litres/litre catalyst/h. at atmospheric pressure good results were obtained but the researches were not completed.

- (5) Work was started on pretreatment with iron pentacarbonyl, diluted with nitrogen, at 50 - 250°C., but again, although the first results were good, the work has not been finished.

Dr. Rottig, of Ruhrchemie, considered that the pretreatment is nothing more than a reduction, and that any carbide formation that occurs is merely incidental. After pretreatment the percentage of metallic iron must be less than 5%, calculated on the total catalyst, or less than 10% calculated on the total iron. The metallic iron plus ferrous oxide must not exceed 50 - 60%, on the total iron. Catalysts which are less reduced than this are active, catalysts more reduced are poor. This has been found to be very important, and as a result the extent of reduction is always measured as a routine test, as follows: The metallic iron is determined in the usual way with mercuric chloride. The (Fe + FeO) is determined by boiling for 2 hours under reflux with 2% acetic acid, and the total iron by dissolving in hydrochloric acid in an atmosphere of carbon dioxide.

Lurgi agree that the pretreatment is nothing more than reduction and always use hydrogen. They say that if the catalyst is intended to produce wax it should only contain some 10% metallic iron, but if benzine is the product required, reduction should be carried as far as possible by increasing the time and the gas rate.

Rheinpreussen, however, take the opposite view, and say that pretreatment is not reduction but consists essentially of carbide formation. No advantage is gained by reducing the catalyst before the pretreatment as iron oxide forms carbide much more readily than metallic iron. But in spite of this general conception of pretreatment Rheinpreussen still think that a further study of the reduction of ferric oxide would be very profitable from the point of view of the synthesis.

They agree with the general view that pretreatment at reduced pressure is no better than at atmospheric pressure, and they also say that their own catalysts precipitated on dolomite as a carrier form no free carbon during pretreatment, which is a great advantage. The K.W.I. agree with this carbide theory of pretreatment and produce thermomagnetic curves to show that during the pretreatment Fe_3O_4 changes to Fe_3C by way of an intermediate compound which is probably a lower carbide. They say that the catalyst only begins to become active when carbide is formed.

Their best catalyst, like the Rheinpreussen catalyst, gives no free carbon during pretreatment.

The Utilization Ratio.

Since the only oxygen product formed during synthesis with cobalt catalysts is water, the ratio of hydrogen to carbon monoxide used up is approximately 2. Iron catalysts normally produce a mixture of carbon dioxide and water as oxygen products, so that the utilization ratio, X , may be anything between 2 and 0.5, the value it would have if carbon dioxide and no water were formed. The utilization ratio is important because its value controls the composition of the residual gas, and if this gas is to be suitable for use in a second stage of synthesis, the utilization ratio must be approximately the same as the ratio of hydrogen to carbon monoxide in the synthesis gas.

Ruhrchemie gave the following account of the factors controlling the utilization ratio. As far as the composition of the catalyst is concerned, the only factor that affects X is the alkali, and the more alkali that is present, the smaller X becomes. The following example was given to illustrate the extent of the alteration that can be produced. Two catalysts of the composition Fe 100: Cu 5: CaO 10: kieselguhr 120 were precipitated with the same amount of alkali, using 10% excess over the theoretical amount of 8% NaOH solution. One sample was washed with 1,200 ml. boiling water/25 g. Fe and the other with only 600 ml. For synthesis with water-gas the first sample gave a utilization ratio of 1.38 and the second 1.18. The kieselguhr as such does not affect X although it may appear to do so since it may introduce alkali into the catalyst.

Of the synthesis conditions, the most important increase in X is that effected by recirculation. The exact change cannot be predicted, but as a typical example, if X is 0.95 for normal synthesis, recirculation will increase it to 1.25. Brabag say that in general those catalysts which normally form a large proportion of wax in the products respond well to recirculation, and the utilization ratio X can be improved in this way up to 1.2. The second Reichsamtversuch was carried out to investigate the effect of recirculation, and for it a recirculation ratio of 2 was used.

X is increased by increasing the proportion of hydrogen in the synthesis gas, and is decreased by conducting the synthesis at a temperature above the best working value, or by running with a lower CO conversion than normal. This latter is not a perfectly general rule, particularly at low temperatures.

The statement that pretreatment with water-gas increases X has not yet been confirmed but may well be true. It is also possible that X is dependent on the pressure, because in one case it was found to be 1.0. at 10 atm. and 1.10 at 20 atm.

General Synthesis Topics.

Some comparison of the performance of a catalyst at atmospheric and medium pressures is important because of the convenience of making a preliminary judgement of a catalyst on the result of a short test at atmospheric pressure. Ruhrchemie said that such tests were useful inasmuch as a catalyst which is active at atmospheric pressure will be more active at medium pressure, and that if one catalyst is better than another at atmospheric pressure it will also be more active at medium pressure.

As far as the effect of pressure on the synthesis is concerned, Lurgi say that the results at 50 atm. are always worse than at 20 atm. At the higher pressure too much of the catalyst surface is covered with products, and what is worse, water is very near its condensation point and damages the iron surface.

Lurgi also point out that the whole question of the second stage is complicated by the fact that the carbon dioxide produced in Stage I has a definitely harmful effect on Stage II. For synthesis with iron catalysts it is not an inert constituent as it appears to be for cobalt, but produces a diminution of activity probably due to oxidation. Lurgi compared water-gas diluted with 30% N₂ and with 30% CO₂ and found that in the second case the yield was 20% less at the same temperature, or to get the same yield 20° higher temperature must be used.

The removal of the carbon dioxide is costly because the benzol has to be removed completely before the Alkaid washing or it is lost and this means that a much bigger active carbon plant would be required than is normally used between the stages.

At the moment therefore, leaving the carbon dioxide in the gas, the conversion U_{CO+H_2} cannot be made to exceed 90%.

The Mechanism of the Synthesis with Iron Catalysts.

Rheinpreussen considers that the synthesis proceeds by way of a labile carbide and say that the deterioration of the catalyst is due to the change of this carbide into a stable one which cannot act as an intermediate compound for synthesis. This change to the stable carbide is favoured by a high proportion of carbon monoxide in the synthesis gas and also by working at atmospheric pressure. The labile, active, carbide may be one of the higher iron carbides, Fe_2C or higher, and magneto-thermal analysis has shown that Fe_2C does change into Fe_3C and also that catalysts contain more Fe_3C towards the end of their lives than at the beginning.

At atmospheric pressure the formation of carbide is a more rapid reaction than the reduction, and the reverse is true at medium pressures. Hence synthesis gas containing a higher proportion of carbon monoxide must be used at medium pressures.

At atmospheric pressure, free carbon is formed very easily, and Rheinpreussen say that their success in this field is due to a large extent to their preliminary work on the different reactivities of α - and γ - Fe_2O_3 .

Finally, they say that for iron catalysts the surface area is not nearly so important as it is for other catalysts.

The K.V.I. obtained the following results by thermo-magnetic work: Their catalyst with 1% Cu. (see p. 122) after pretreatment with carbon monoxide at reduced pressures contained pure Fe_2C . The catalyst with 20% Cu. (see p. 122) after pretreatment with synthesis gas contains Fe_3C , Fe and Fe_3O_4 . Yet both samples are equally active. During synthesis the amount of carbide decreases in the first case but stays constant in the second. The oxygen content of the catalyst increases during synthesis, and this corresponds to a fall in activity.

If synthesis is attempted at medium pressure without pretreatment, no carbide is formed and the catalyst is inactive.

Catalysts for Synthesis at Higher Temperatures.

Before interest in Germany turned towards finding an iron catalyst which could be used in the existing medium pressure plants, Ruhrchemie developed several iron catalysts which would work very successfully at 250°C. and higher temperatures. One of these was to be used in the plant designed for the Societa Italiana Carburanti Sintetici at Arezzo. It had the composition Fe 100: Cu 5: CaO 10: kieselguhr 150, and was prepared by rapid precipitation from the nitrates with potassium hydroxide solution at the boiling point. After reduction in dry hydrogen for one hour at 300°C., synthesis was carried out at 20 atm. pressure, with water-gas, recirculation ratio 2.5, and a space velocity of 90. The temperature only required raising from 251 to 257°C. during the course of 120 days, but Ruhrchemie say that on account of the high proportion of kieselguhr it was possible to use it over a wide temperature range. In the experimental work with this catalyst, on which the Arezzo project was based, a two-stage pilot plant was worked to an 83% conversion and gave a yield of liquid and solid products of 115 g./N.cu.m. From this it was calculated that the yield would be at least 140 g. if the plant were operated to a conversion of 93%. It was a wax-forming catalyst, the products containing 35% wax, of which 17% was hard wax of boiling point above 460°C.

Ruhrchemie then found that the expensive step of precipitation with potassium hydroxide could be avoided and the catalyst precipitated with sodium carbonate so long as the sodium salts were washed out thoroughly and a little potassium carbonate or hydroxide incorporated with the washed precipitate. Such a catalyst produced as little methane as a catalyst precipitated with potassium hydroxide. They also found that if they boiled the kieselguhr for a short time with the sodium carbonate solution that was to be used for the precipitation, all the good effects were obtained which Lurgi had previously achieved by adding waterglass to their catalysts (see p. 124). Ruhrchemie claimed that their method gave more effective catalysts and was also cheaper. They always used the same kieselguhr as is used in the manufacture of cobalt catalysts, but they have tested kieselguhr containing both calcium and iron, and they are perfectly good for the preparation of iron catalysts. No kieselguhr specially suitable for iron catalysts has been found.

As an example of one of their best high temperature catalysts, Ruhrchemie gave the following example. A preparation of the composition Fe 100: Cu 5: CaO 30: kieselguhr 100 was carried out on the semi-technical scale. A solution was first made up to contain 6 kg. iron with the correct amount of copper and calcium in 120 litres condensate water, and heated to boiling. At the same time 22 kg. soda was dissolved in 190 litres condensate water and also boiled. The kieselguhr, 6 kg. was stirred into this solution and boiled for 30 seconds. The solution of the iron was then added with rapid stirring during the course of 2 minutes. A further 3 kg. soda was added to the mixture and the stirring continued for 20 seconds. The precipitate was then filtered off on a filter press and washed for 30 minutes with hot condensate water. The filter cake was put through an extrusion press and the resulting dried catalyst was in a very hard and physically suitable form.

Using ordinary water-gas with 13% inert constituents, the results shown in Table 44 were obtained for synthesis at 20 atm.

Table 44.

Synthesis with Ruhrchemie's
High Temperature Iron Catalyst

Space Velocity, per h.	100	200	284
Recirculation Ratio	2.7	2.4	2.0
Temperature, °C.	246	267	280
Conversion, U	72	68	69
H ₂ /CO in water-gas ^{CO + H₂}	1.22	1.19	1.23
H ₂ /CO used up, X,	1.14	1.11	1.13
CH ₄ as % of CO converted	6.10	8.10	15.6
Yield g./N.cu.m. (CO + H ₂) including Gasol	113.7	96.4	76.3
Benzin, b.p. 200°C. in liquid products, %	33	41	62

This table also shows how the proportion of benzine in the products increase very rapidly as the temperature is increased.

For synthesis at higher temperatures Rheinpreussen developed a catalyst of composition Fe 100: Cu 5: K_2CO_3 0.25, precipitated by sodium hydroxide and containing no kieselguhr. Synthesis was done with gas with $H_2/CO = 0.5$, but work on these lines has now been stopped.

Ruhrchemie's present opinion about synthesis with such catalysts at $250^\circ C$. and above, is that it is less satisfactory on economic grounds, than synthesis with the best low-temperature iron catalysts. In particular, the higher working temperature means that both plant costs and working costs are higher.

Catalysts for Synthesis at Low Temperatures.

As already mentioned, the shortage of cobalt in Germany during the war made it very important to develop an iron catalyst which could be used in the existing medium pressure plants, i.e., one which would work at temperatures below $225^\circ C$. The position up to the winter of 1943-4 is summed up by the 'Reichsamtversuch', a comparative experiment arranged by the Reichsamt für Wirtschaftsausbau in which the six best iron catalysts available were tried out simultaneously at the Brabag works at Schwarzheide. Since that time a great deal of progress has been made and in this section an account of the best modern catalysts is given, together with some particulars of several of the Reichsamtversuch catalysts which were not previously available.

Ruhrchemie consider that catalysts must be very dense, and hence contain little kieselguhr, if they are to be active at low temperatures. Their best low temperature catalyst had the composition Fe 100: Cu 5: CaO 8: kieselguhr 30 and was prepared as follows. A solution of iron, copper and calcium nitrates was made up to contain 50 - 55 g. Fe/litre and with Fe : Cu : CaO in the ratios 100 : 5 : 10, the excess CaO over the amount required in the final catalyst being used to allow for incomplete precipitation. This solution is heated to $98^\circ C$. and run into a boiling solution of sodium carbonate of strength 90 - 100 g. Na_2CO_3 /litre which is stirred vigorously. The amounts of the solutions are chosen so that after the precipitation the pH is 6.8 - 7.0. The calculated amount of kieselguhr is then stirred in, using preferably a sample of low density which has been heated to $700^\circ C$. The mixture is filtered and washed with

hot distilled water till the content of NaNO_3 in the finished catalyst is about 0.5 - 0.7% based on iron. From 200 to 220 litres water per kg. Fe are generally sufficient. The wet filter cake is then impregnated with 3.0 to 3.5% KOH, calculated on Fe by repulping it in a solution of KOH and filtering. A concentration of 6.0 g. KOH/litre in the mother liquor is usually sufficient to get the correct amount of KOH in the filter cake. After filtration, the cake is formed in a suitable manner and dried at 110°C .

The catalyst is hard and resistant to abrasion. It is reduced at 300°C . for 1 hour with a mixture of 75% hydrogen and 25% nitrogen. The content of metallic iron after reduction should not exceed 8 - 10% and the metallic plus ferrous iron should not exceed 60 - 70% of the total iron present.

The utilization ratio, X, of this catalyst increases from 1.05 for the first month of syntheses to 1.20 after five months, but it is considered that by making small changes in the catalyst these figures could be improved. Small changes in the amount of kieselguhr could increase X a little, and a slight reduction in the amount of alkali might be required to make the catalyst suitable for use on the full-scale.

Dr. Kölbl, of Rheinspreussen, gave the following account of the best iron catalyst he has developed for medium pressure synthesis. Normally it has the composition Fe 100 : Cu 1 - 10 : dolomite 50 - 100 : K_2CO_3 0.1 - 3, but for work with gases rich in carbon monoxide the dolomite may be replaced by kieselguhr. In general, dolomite is a very satisfactory support for medium pressure iron catalysts as it promotes the formation of wax, prevents the formation of carbon and gives a very hard catalyst. A band of dolomite containing no sulphur or phosphate is chosen in the mine, and the material from this band is roasted at 700°C . and ground to a fine powder. But a synthetic dolomite made simply by mixing magnesium and calcium carbonates was just as good.

The catalyst is prepared as follows:- The iron is dissolved in nitric acid to give a 10% solution, the copper nitrate added, the solution boiled, the dolomite added and the precipitation carried out by adding boiling 10% sodium carbonate solution. It is essential that these operations be carried out in the order given above. After filtration

and washing, the potassium carbonate, dissolved in water, is stirred into the wet filter cake, which is dried and granulated to 1 - 3 mm. pieces. It is not formed by extrusion through dies. A preparation has been carried out on the large scale in the catalyst factory of Brabag and was perfectly successful, the filtration being easier than for the normal cobalt catalyst.

Pretreatment is done at atmospheric pressure, 240°C ., in synthesis gas, $\text{H}_2/\text{CO} = 2$, which is carefully freed from carbon dioxide but need not be dried. The gas is passed at 10 times the normal gas rate.

Synthesis is carried out at $205 - 215^{\circ}\text{C}$. and 3 - 10 atm. with synthesis gas having $\text{H}_2/\text{CO} = 2$. No recirculation is necessary, in fact, it is disadvantageous as it reduces the proportion of wax in the product slightly. Apart from this, the use of synthesis gas is preferable to that of water-gas as there is no formation of carbon, less formation of carbon dioxide, the presence of which makes the active carbon stage of the condensation more difficult, and the wax produced is said to be more suitable for oxidation. Also, water-gas would require a temperature some 15° higher.

Worked in two stages, with a space velocity of 500 - 1000/h. for Stage I, the yield is 150 - 155 g./N.c.u.m., excluding methane, which corresponds to a production of 5.5 t. products/full-scale reactor/day. The life of the catalyst is 6 months or more. The utilization ratio, X , is 1.5 and is better in Stage I than in Stage II. It is known to depend on the alkali in the catalyst when working with gas rich in carbon monoxide, but it is not known whether there is any such effect when working with synthesis gas. The methane formed amounts to 5 - 10% of the products, which is less than the amount formed by medium pressure synthesis with a cobalt catalyst. The products are in general similar to those obtained from cobalt catalysts at atmospheric pressure, in particular, in having only a small proportion of wax. The wax can be increased by using more alkali in the catalyst, a higher proportion of carbon monoxide in the synthesis gas, or by working at higher pressures. In this latter case, however, more organic oxygen compounds are produced.

The catalyst used by Rheinpreussen in the Reichsamtversuch at Schwarzheide in 1915 was an earlier and less effective catalyst of this type, of composition Fe 100 : Cu 7.5 : dolomite 50 - 65 : K_2CO_3 2, pretreated in synthesis gas at reduced pressure. The yield was not good as the experiment had to be done in one stage.

Work at the K.W.I. had been on rather different lines, and their best catalyst for synthesis at low temperatures is one containing no kieselguhr or other support. It has the composition Fe 100 : Cu 20 : K_2CO_3 1 and is made from a mixture of 75% $FeCl_2$ and 25% $FeCl_3$. An amount of these salts corresponding to 50 g. iron is dissolved in water, made up to 3 litres, the solution heated to 70°C. and precipitated rapidly at that temperature by the corresponding amount of sodium carbonate dissolved in 1 litre water. A slight excess is used so that the solution is just alkaline at the end of the precipitation. The mixture is then heated to 100°C., filtered, washed free from alkali, the potassium carbonate added in the usual way and the mixture evaporated and dried at 105°C. No special precautions against oxidation are taken during the drying and, in fact, drying in air is better than in an inert atmosphere. More ferric salt must be used in the original mixture if it is desired to dry out of contact with air. The dried catalyst is granulated on a sieve.

It is pretreated with synthesis gas, $H_2/CO = 2$, at 225°C. and atmospheric pressure, at a space velocity of 500/h. The gas is neither dried nor freed from carbon dioxide. This pretreatment lasts for 2 days. At the end of this period it may become inactive, on account of wax formation, and if so, it must be extracted with high boiling Kogasin (230 - 300°C.) at 225°C., and the 2 days pretreatment repeated. After a further extraction it is ready for synthesis.

Up to now no attempts have been made to start synthesis at medium pressure directly but two weeks work at atmospheric pressure has always been done first (for details see p. 140). After this two weeks, the pressure is increased to 2 atm. and synthesis continued for another 2 weeks at 212°C., using water-gas. The pressure is then put up to 10 atm. and synthesis can be done at a constant temperature of 198 - 200°C. for three months. No extraction with solvent is necessary although much more wax is being formed than at atmospheric pressure. The average yield is 143 - 148 g./N. cu. m., including methane, which latter is, however, vanishingly small. The utilization ratio $X = 0.7 - 0.8$. The effect of recirculation has not yet been tried.

A good medium pressure catalyst is also obtained by reducing the 20 parts of copper in the above preparation to 1 part. When this is done the pretreatment is best if carried out with carbon monoxide alone, at 1/10 atm.

pressure. The synthesis temperatures are rather higher than if 20 parts of copper are used.

Referring back to the Reichsamtversuch, the K.W.I. said that the experimental reactor used at Schwarzheide had a wider tube than their own reactors, and as a result, their first catalyst gave too much liquid and gaseous products. This was rectified by preparing a second catalyst containing more alkali and this one ran successfully for 3 months. A third catalyst, with still more alkali, was tried for 3 weeks.

Lurgi point out that the K.W.I. catalyst produced a great deal of C_2 hydrocarbons and that these are included in the yields quoted. In practice these hydrocarbons could not be recovered and hence the actual yields would be lower. The final gases contain 40 - 50% CO_2 and 1 - 2% C_2 hydrocarbons, and if these are to be recovered the CO_2 must be removed by Alkaziid washing, which in turn causes losses of hydrocarbons. Thus the recovery of C_2 is always too dear.

Although the results obtained in the Reichsamtversuch with all the six catalysts are well-known, the compositions of the Lurgi, the Brabag and the I.G. Farben catalysts were not available. These have now been obtained.

The Brabag catalyst had the composition Fe 100 : Cu 20 : Zn 20 : K_2CO_3 1, the zinc being in the form of zinc oxide. It was a normal precipitated catalyst, made from the nitrates and sodium carbonate. It was pretreated with water-gas at 235 - 240°C. at atmospheric pressure. When the production of carbon dioxide falls off the pretreatment is considered to be finished, and it usually requires some 48 hours. If the pretreatment is stopped too soon, the catalyst disintegrates during synthesis.

The first of these catalysts used in the Reichsamtversuch was too soft, disintegrated, and came out of the reactor with the products. The second attempt was spoilt because the temperature was increased too rapidly and deposition of carbon occurred. The third attempt was successful.

The Lurgi catalyst had the composition Fe 100 : Cu 10 : Al_2O_3 9 : SiO_2 30 : K_2CO_3 2, the K_2CO_3 being added to give 2% K_2O . Subsequent Lurgi catalysts had 25 parts copper but behaved essentially in the same way as the above except that the utilization ratio was improved. These catalysts are prepared by precipitation with sodium carbonate from a hot solution of the mixed nitrates; freshly precipitated silica,

from waterglass and dilute mineral acid, is then stirred in and the mixture filtered, washed and impregnated with potassium carbonate.

Lurgi say that pretreatment may equally well be done with hydrogen, water-gas or diluted carbon monoxide but they prefer hydrogen as this avoids all trouble due to synthesis setting in, bolting and carbon formation. For full-scale working hydrogen would be the obvious choice for two reasons. Firstly, if water-gas were used the treatment would have to be done in the reactor itself because of the danger of synthesis setting in, and the reactors are not capable of being used at temperatures high enough for the pretreatment. And secondly, on account of the very high gas rate required, the water-gas would have to be recirculated and before it could be passed through recirculation pumps all the synthesis products would have to be scrubbed out of it.

The pretreatment actually used is carried out with hydrogen at a space velocity of 1,000/h. for 1 - 3 hours at 280°C., the exact time depending on the alkali and copper content. The reduction is slower the more alkali present. The temperature required varies from 250 to 300°C., according to the amount of copper present, and in its absence temperatures above 300°C. are required. If pretreatment is done with gases containing carbon monoxide, under certain conditions temperatures as low as 180 - 200°C. may be used. Temperatures above 300°C. always give bad results.

The catalyst Lurgi used in the Reichsamtversuch started synthesis successfully at the first attempt and worked to a utilization ratio $X = 0.7$ without recirculation or 1.0 with recirculation. Their latest catalyst gives $X = 1.3$ and they are confident that this could be increased to 1.6 if necessary. Ruhrchemie and Rheinpreussen got as good a utilization ratio but only at the expense of producing more methane. The silica gel is the factor which gives a good utilization ratio.

The alkali silicate, that is, the K_2O plus an equivalent amount of silica, is responsible for the good physical form and the long life. It stabilizes the paste during the preparation of the catalyst and prevents thixotropic liquefaction, and as a result, the catalyst threads after drying are hard and break like glass. A normal iron catalyst becomes more and more reduced during continued synthesis but this alkali silicate catalyst does not.

The life is very good; thus, during the 90 days run at Schwarzheide the temperature had only to be raised 2°, from 216 to 218°C. to maintain activity.

The I.G. Farben low-temperature iron catalyst was a melted catalyst of the composition Fe : Al₂O₃ : CaF₂ : K₂O the calcium fluoride being added to increase the formation of light hydrocarbons. It is a very remarkable fact that such a catalyst was just as active as the other catalysts used in the Reichsamtversuch, all of which were made by precipitation and pretreatment under carefully controlled conditions. To produce wax, the calcium fluoride is left out, and preparations of the composition Fe : K₂O : MgO or Fe : K₂O : Al₂O₃ are used, the activating oxides being melted with the iron in oxygen. At 230 - 250°C. they produce products containing more than 60% wax. The cost of preparation is about the same as that of precipitated catalysts.

Catalysts based on Luxmasse

Ruhrchemie say that it is difficult to make such catalysts hard enough for use on the full-scale. They are essentially catalysts which tend to form light products and not wax, and they require a high temperature. They are considered on all these grounds to be inferior to the low-temperature catalysts already referred to.

As an example, the catalyst Fe 100 : Cu 3.5 : bleaching earth 100 : kieselguhr 10 may be described, as it was prepared and tested by Ruhrchemie in 1940. A volume of 1,100 ml. 10.3% KOH, specific gravity 1.085 was heated to boiling, 3.5 g. kieselguhr 120 added and the boiling continued for 1.5 minutes. Then, with continuous intensive stirring a suspension of 200 g. Luxmasse (35 g. Fe), 35 g. bleaching earth (Granosil) and 10.3 ml. copper nitrate solution (1.25 g. Cu) in 500 ml. hot distilled water was added and heated with continued stirring till boiling began. The mixture was then filtered, washed with three portions, each of 200 ml., of distilled water at 90°C., and the filter cake dried at 110 - 115°C. After granulation in the usual way the bulk density was 500 g./litre.

Synthesis was started with water-gas at atmospheric pressure, at a space velocity of 100/h., and the temperature was increased until a contraction of 20% was obtained. The pressure was then put up to 15 atm. and synthesis carried out with a recirculation ratio of 1.5 to 2.5, at 255°C. The utilization ratio, X, was 1.27 and the con-

version, 11, 60%. The yield, calculated for a 90% conversion, was 95 g. liquid products and 21 g. gasol. per M. cu. m., and the liquid product had the following boiling range: - below 200°C. 55%, 200 - 320°C. 31%, max above 320°C. 50%. The product boiling below 200°C. had an octane number of 72.

Iron Catalysts for Gas Rich in Carbon Monoxide

All iron catalyst development done by Ruhrchemie was in the direction of catalysts to work with water-gas, and they had no immediate interest in catalysts suitable for gases containing a higher proportion of carbon monoxide. Using such gas, more olefines are produced, but at the cost of a higher synthesis temperature, which means bigger plant costs and working costs. Carbon formation and dark coloured wax also occur. The effect of recirculation on these matters was not known.

The essential requisite for synthesis with gas rich in carbon monoxide is a supply of cheap oxygen, because suitable synthesis gas can only be made by gasification with oxygen. Working in this way, I.G. Farben produced suitable synthesis gas economically.

An example of a very successful catalyst for a gas with H_2/CO 2 : 3 is the R.H.I. catalyst of composition Fe 100 : Cu 1 : K_2CO_3 0.25, prepared by dissolving iron in nitric acid under fixed conditions such that a little ferrous nitrate is formed, and then precipitating in the normal way. It works at 235 - 245°C. and 10 - 15 atm.

Lurgi consider that if such a gas could be prepared as cheaply as ordinary water-gas, the best ratio of H_2/CO is 1 as it gives more wax, more olefines and less methane than ordinary water-gas. But they consider that gases richer in carbon monoxide are not desirable.