

Cobalt Catalysts

Composition.

The reasons for Ruhrchemie's decision to change the composition of the catalyst from Co 100: ThO₂ 18: kieselguhr 100 to Co 100: ThO₂ 15: kieselguhr 200 and subsequently to Co 100: ThO₂ 5: MgO 8: kieselguhr 200 have already been discussed (see B.I.O.S. Final Report No. 447, Item No. 30) but the following additional information was obtained. Ruhrchemie admitted that a Co 100: ThO₂ 18: kieselguhr 100 catalyst made with the kieselguhr S.11 was more active than subsequent catalysts, and gave, in fact, an average yield of 120 g./N.cu.m. over the first 4,000 hours of its life in the 'Rauxelerversuchsofen' - the reactor in which the work was done on which the guarantees given by Ruhrchemie to the licensees were based. But in spite of this the change was made to the present more dilute catalyst not only on account of the failure of the supply of the kieselguhr S.11 but also because the more diluted catalysts are easier to use in the present type of reactors and in general are more suitable for these reactors than catalysts with less kieselguhr or higher density. Thus if a sample of the present catalyst is compressed and used for synthesis at the same temperature and space velocity, it gives more methane than the more dilute normal sample even though the gas rate may be only 0.5 litre/g.Co/h. Rheinpreussen, who had previously been in favour of retaining the old catalyst with its high cobalt density now admit that the modern mixed catalyst is the most satisfactory. But they would like to have this prepared in a harder form on account of troubles with dust during revivification of the catalyst by extraction with solvents.

Brabag say that the real reason for abandoning the Co 100: ThO₂ 18: kieselguhr 100 catalyst was its softness, which would not stand up to repeated extractions with solvent but broke down to dust which caused blockages and gave trouble

in emptying the reactor. The catalysts containing magnesia give poorer products - less wax and more methane - but their mechanical strength was the factor which decided the issue in their favour.

Ruhrchemie determined the effect of varying the amounts of thoria and magnesia in the catalyst on the life and activity in the following way. Each preparation was run for 2,800 hours starting at 185°C., treating with hydrogen after 700 hours and again at 2,200 and 2,500 hours. The temperature was increased to 192°C. at 950 hours, 193°C. at 1,900 hours, and to 194°C. at 2,200 hours. The figures given in Table 6 for output of products are the total output taken as a percentage of the output from the best sample. It is remarkable how small an amount of thoria is sufficient to make a Co: ThO₂: MgO: kieselguhr catalyst perform satisfactorily.

Table 6.

Effect of Composition on the Performance of the Catalyst

Catalyst Composition				Output of Products %
Co	ThO ₂	MgO	kieselguhr	
100	5	10	200	100
100	3	10	200	99
100	2	10	200	99
100	1	10	200	95
100	0.5	10	200	95
100	-	10	200	92
100	-	15	200	92
100	15	-	200	90

As far as the present large scale catalyst manufacture is concerned, the usual variation in composition is within the limits.

ThO₂ 4.9 - 5.2% (on metallic cobalt)
MgO 7.5 - 8.5%

The figure for MgO is not critical, and anything from 6 to 10% would be satisfactory. But the ThO₂ should be as near 5% as possible because of its role as protector against impurities. The same composition has been found to be best both for atmospheric and medium pressure synthesis and Ruhrchemie supply the same catalyst for both purposes.

Kieselguhr.

Ruhrchemie consider that any kieselguhr of sufficient purity, suitable density etc. should be suitable for catalyst manufacture. The form of the individual diatoms is not important.

The two most important impurities are iron and calcium. The iron increases the production of methane and carbon dioxide, and although it is the soluble iron that is most harmful, the insoluble iron can also become activated by the reduction so as to exert a bad effect in the same direction. It must be remembered however that the iron is only one of the various factors which determine methane formation.

The calcium by itself is not harmful, but during the catalyst preparation in the factory it becomes precipitated as sulphate. This is reduced to sulphide when the catalyst is reduced and this poisons the catalyst.

The only purification that is done on a large scale is calcination in a rotary furnace. This gives a denser product than calcination in the laboratory, which latter treatment therefore yields a superior kieselguhr.

Purified Guhr' means kieselguhr that has been boiled with 5% nitric acid and then calcined at 500°C. (boiling the previously heated kieselguhr with the nitric acid gives worse results). Results on the large plant do not justify the expense of this treatment on the large scale.

Ruhrchemie obtained their kieselguhr from the Vereinigte Deutsche Kieselgurwerke, Hannover, and fixed the specifications given in Table 7 for it.

Table I.

Specification for Kieselguhr.

		Gießguhr ^x	Röstguhr ^y
1) Bulk Density	g./litre	120 - 150	60 - 120
2) Sand content (Schwim-Härtest)	%	2	2
3) Acid-soluble constituents. The following values must not be exceeded when 1 part of kieselguhr is boiled for 1 hour with 5 parts 2% HNO ₃			
	Fe	1	1.7
	Al	0.1	0.4
	Ca	0.2	0.2
	SO ₄	0.4	0.6
4) Loss of weight on heating. After 1 hour at 1,000 - 1,050°C. the loss should not exceed	%	0.5	2.5

^x See B.I.C.S. Final Report No. 447, Item No. 30, p. 3.

The kieselguhr used in the Wabag catalyst factory was air-blown and roasted at 1,000°C., but for small scale work they purify raw kieselguhr by roasting to 600 - 700°C., air-blowing, and then washing in counter-current with conc. H₂O₂ either at room temperature or rather warmer. In this way a kieselguhr is obtained which is as good as the original S.11. Dr. Sauter thinks that this purification would pay on the large scale as the iron in the kieselguhr is got rid of once and for all and will not interfere in the regeneration. The kieselguhr could also be used again.

A little more information was also obtained about the kieselguhr S.11 which was used in the early days of the synthesis and which gave better results than any subsequent kind. This kind of kieselguhr occurs at the top of the deposits and contains no organic matter or other impurities. It only requires air-blowing.

The K.W.I. consider that the only function of the kieselguhr is to increase the surface area of the catalyst and to allow the wax formed in the synthesis to drain away more easily.

Preparation.

The method used at the Ruhrchemie factory has already been described (see C.I.O.S. Report, Item No. 30, File No. XXVII - 69) but the following additional details were obtained. Previously the used catalyst was carefully oxidized before grinding to a paste with hot water, but nowadays the oxidation is omitted. The pulping is done with a high-speed stirrer but it is considered that a ball-mill would be better.

For the actual precipitation the amount of sodium carbonate was so chosen that the mother liquor, after precipitation is finished, contains 1 - 2 g. Na_2CO_3 /litre and 6 - 8 g. NaHCO_3 /litre.

The Wintershall catalyst factory used essentially the same method as Ruhrchemie, but at the Brabag factory the following procedure was adopted. They dissolve the used catalyst in nitric acid, filter off the kieselguhr, precipitate the iron and calcium, and then precipitate the whole of the cobalt with Na_2CO_3 . The cobalt carbonate is redissolved in nitric acid and the right amount of magnesia and thoria added. Although this method of working requires twice the amount of nitric acid that the Ruhrchemie method employs, the Brabag consider that their method of precipitating the whole of the cobalt is superior as it removes organic impurities. A comparative test done at Ruhrchemie on the two methods gave inconclusive results.

Ruhrchemie developed a method of preparing catalysts by precipitation from solutions of sulphates (see German Patent Application R.104,999 15.IV.39) and they said that these catalysts were perfectly satisfactory provided the precipitate was washed carefully with dilute alkali. They had not developed this method for their own use, but thought that firms who had no cheap source of nitric acid might be interested in it.

Forming the Catalyst.

Normally Ruhrchemie prepared some 20% of their catalyst in 1 - 2 mm. granules and the rest in 2 - 3 mm. granules.

The smaller size was preferred by Essener Steinkohle. For atmospheric pressure reactors either size, or a mixture of the two may be used, but for medium pressure double tube reactors a mixture is bad since the different sized particles tend to become segregated.

Ruhrchemie have investigated a number of other ways of producing the catalyst in pieces of a suitable size and shape. Referring to the 'Eirichkorn' catalyst (see B.I.C.S. Final Report No. 447, Item No. 30) they said that this was too dense and formed too much methane. Since it was very hard it behaved excellently in the plant, but there was a rather serious difficulty about the preparation, namely that it could never be prepared in a close range of sizes. Normally only 60% falls in the 2 - 3 mm. range.

As far as thread catalysts are concerned, it was stated that there is very great difficulty in preparing fine threads, of the order of 2 mm. diameter, on the large scale as the fine holes of the press get blocked with bits of cloth, wood, etc., from the filters. Ruhrchemie thought it impracticable to make thread finer than 5 - 6 mm. Wintershall tried to overcome the difficulty by using a device for clearing the holes with an array of plungers, but this was not very successful.

The greatest success was obtained with the 'Schiffchen' catalyst, so called because the final pieces were in the form of little boats. This was made on a machine constructed by winding large numbers of strips of iron, shaped as shown in Figure 1 (a), round the outside of a drum of some 2 m. diameter. These strips are separated by unserrated strips so that a very large number of cells of the shape shown in Figure 1 (b) and of size 2 x 2.5 mm. are formed. Catalyst paste is squeezed into these cells at the lower part of the drum, and as the drum rotates continuously they are carried up, dried at the top and then the dry and formed pieces of catalyst fall out of the cells. The serrated strips extend all the way round the drum whereas the unserrated ones only extend round the lower third of the circumference and they do not rotate with the drum. As a result the cells containing the catalyst are open at the sides during the drying at the top of the drum.

The catalyst formed in this way gives very little dust and is very hard. This is probably due to the fact that there is so little dust incorporated in the catalyst paste,

because this is one of the main causes of mechanical softness of the ordinary catalyst factory granules.

Ruhrchemie were so pleased with the Schiffchen catalyst that they were considering making it on the full scale. The plant necessary would be very much smaller and more compact than the present drying and granulating plant.

To go back to the normal Ruhrchemie method, they said that the specification was always laid down that the finished catalyst should contain 6 - 8% moisture. There is no special merit in having this moisture present, and it is only specified so as to discourage drying at too high a temperature. If too high a temperature is used cobalt oxide is formed and this cannot be reduced under the normal catalyst reduction conditions. For catalysts with 200 parts kieselguhr, 120°C. is a safe drying temperature, but catalysts with less kieselguhr oxidize more easily. This is particularly noticeable for the catalysts containing only 25 parts of kieselguhr and having manganese as activator and these preparations require very careful drying (see p.32). But here the manganese may catalyse the oxidation by acting as an oxygen carrier.

The bulk density of the finished catalyst is a matter of very great importance and Ruhrchemie said that this was influenced by a number of factors. Thus it depends on the amount of catalyst dust incorporated, increasing as the amount of dust added is increased. It also depends on the nature of the kieselguhr, calcined kieselguhr '120' - Glühgur - giving a denser catalyst than Röstgur (see Table 7 and B.I.O.S. Final Report No. 447, Item No. 30 for a description of these kieselguhrs). Long continued mixing before extrusion and drying increases the density, and so does squeezing through the extrusion press. Drying in large cakes gives a very light catalyst. The large scale preparations of the Co 100: ThO₂ 5: MgO 8: kieselguhr 200 catalyst made with Röstgur had a density of 330 g./litre whereas laboratory preparations always had a density 10% less.

Finally it may be mentioned that while marked deterioration due to storage of unreduced catalyst for a period of years has been observed at the Fuel Research Station, Greenwich, Ruhrchemie, said they had never observed such an effect.

Catalyst Losses

In considering costs of catalyst manufacture prepared by Ruhrchemie it must be remembered that each licensee possessed a stock of cobalt metal which was kept at the catalyst factory. As each batch of used catalyst was returned to the factory it was dissolved separately, the weight of cobalt estimated, and any loss made up by addition of cobalt from the stock of the licensee concerned. Hence no figures for 'loss' occur in the cost sheets. Actually, in the catalyst factory losses occur both in the extraction of cobalt and thorium from used catalysts and in the preparation of fresh catalyst from the extracted materials. In addition to these losses at the factory losses also occur at the synthesis plants and during transport, and data for this, supplied by Ruhrchemie, is given in Table 8.

Table 8.

Losses of Cobalt and Thorium

	Co	ThO ₂
Loss during recovery	0.94%	9.8%
Loss during preparation	2.36	0.2
Loss at the synthesis plants, etc.	1.37	6.2
Total Loss	4.67	16.2

In estimating the effect of these losses, the price of cobalt metal, 99% Co, may be taken as RM. 8.00/kg., thorium, 64 - 65% ThO₂ as RM. 18.00/kg. and kieselguhr as RM. 0.14/kg.

Laboratory Tests of Catalyst Activity.

The following routine test were carried out by Ruhrchemie to decide whether the activity of a sample of catalyst was satisfactory. The tests were conducted at 185°C. throughout and with synthesis gas containing 18 - 20% inerts.

For the first 4 hours of synthesis a good catalyst always forms methane, with a contraction $K = 60\%$. After 36 hours the methane formation should come to a stop and the contraction should have increased to 70% . For the next 200 hours the contraction should not fall below $67 - 68\%$. At this stage a bad catalyst can be detected either by failure to form methane during the first few hours, or by the contraction falling too rapidly.

Sometimes the test is carried on till 500 hours, at which stage the contraction should be at least 66% and the yield over the whole period 128 - 130 ml. liquid products/cu.m. synthesis gas.

These short tests donot allow a prediction of the life of the catalyst to be made, and for that purpose have to be extended to 1,000 hours. At that time the contraction must not be less than 60% for a satisfactory catalyst.

The above details refer to the Co: ThO_2 : MgO: kieselguhr catalysts. For catalysts containing no magnesia the test is run as described up to 530 hours when the contraction should be 55% . Hydrogen revivification is then done, which should bring the contraction back to 70% . The test is then continued for a further 400 hours, at the end of which period the contraction should not be less than 58% .

If these tests show that a catalyst is unsatisfactory, the percentage of the total amount of cobalt that is reduced to metal - the so-called reduction value - is determined, and if this is normal a complete chemical analysis is done to see whether any gross error has been made in the preparation.

Ruhrchemie consider that the performance of a catalyst cannot be predicted with any accuracy by measuring the rate of formation of wax, although there is a rough correlation between this and the life.

Special Catalysts for the Production of Wax.

Ruhrchemie found that cobalt catalysts with manganese as activator produced a particularly high proportion of wax, and they found that the best composition was Co 100: Mn 15: kieselguhr 12.5. This catalyst was prepared as follows:-

A solution of cobalt and manganese nitrates containing 25 g. Co and 3.75 g. Mn in 500 ml. distilled water is boiled and run quickly into a boiling solution of 62 g. anhydrous sodium carbonate in 750 ml. distilled water, which is stirred vigorously. Immediately after the precipitation 3.2 g. kieselguhr is stirred in, using preferably a kieselguhr that has been washed with hot nitric acid and then heated to 500 - 600°C. The mixture is filtered at once and washed with 3 litres hot distilled water. The activity of the catalyst is diminished if too high a temperature is used during drying and it is best to dry the catalyst at 60 - 75°C. in the open air, using an electric heater. Reduction is done at 400°C. for one hour, with a velocity of 300 litres gas/h. for 50 ml. catalyst, using a mixture of 75% hydrogen and 25% nitrogen.

Synthesis is carried out at 10 atm. pressure with ordinary synthesis gas, $H_2/CO = 2$ using a gas rate of 10 litres/h./100 ml. catalyst. The temperature at the beginning was 160°C., but was increased during 5 months to 175°C. A yield of 120 g./N. cu.m. was obtained, corresponding to a conversion of carbon monoxide of 75%. During this time the composition of the products changed as shown in Table 9.

Table 9.

Products obtained using the Cobalt -
Manganese Catalyst.

Time, hours.	1-552	662-1099	1099-1720	1720-2240
	%	%	%	%
Benzin -200 °C	21.0	13.9	6.1	5.0
Diesel Oil 200-320 °C	20.5	16.0	14.7	16.7
Soft Wax 320-460 "	25.8	22.9	23.8	21.5
Hard Wax 460- "	32.7	47.2	55.4	56.8
Total Wax 320- "	58.5	70.1	79.2	78.9

This catalyst cannot, unfortunately, be tried on a large scale as it is far too soft, and in addition, its use would involve difficulties due to its sensitivity to overheating during drying, its tendency to form carbon at the beginning of its life, and the precipitation of manganese dioxide during regeneration, which would clog the filters.