

Reduction and Revivification

Reduction.

Ruhrchemie consider that although the top of a catalyst bed is better reduced than the bottom - there is a difference of 3 - 5% in the reduction value - this will not affect the activity. They base this view on the general opinion that oxidation-reduction equilibrium is reached in the catalyst during synthesis. During the first 14 days synthesis in the full scale reactors the yield increases to a maximum and this is said to be due to an increase in the reduction value. After this the yield drops slowly and so does the reduction value, the latter decreasing from some 55% to 35 - 40%.

In conformity with the above point of view, the reduction value is no longer considered as giving any indication of the activity to be expected from a catalyst except insofar as it shows whether a catalyst has been reduced too much. If this is so, and the reduction value is very high, the activity of the catalyst is good initially but rapidly falls off. It is always better to start with a moderate activity.

It is generally stated that the reason for carrying out the reduction with hydrogen that has been carefully freed from water-vapour and carbon dioxide and which is passed at a high rate, is to get reduction completed as quickly as possible so as to avoid sintering. Dr. Michael, of I.G. Farben considered that the sintering is due not so much to the mere effect of temperature as to a recrystallization caused by alternate oxidation and reduction of the catalyst caused by moist hydrogen.

For reduction on the large scale, Brabag used 90% hydrogen and hence use lower temperatures, 360 - 370°C., than Ruhrchemie, who use 400°C. and 75% H₂. Although it is sometimes stated that the reduction temperature at Ruhrchemie is 420 - 450°C. it must be emphasized that this only refers to the temperature of the hot hydrogen entering the reduction vessel.

After reduction, Ruhrchemie cool the catalyst by circulating nitrogen. Wintershall drop the hot catalyst into a box fitted with cold water pipes and cool it in this way while maintaining a slow circulation of nitrogen.

Reducibility.

The effect of the catalyst composition on the reducibility was investigated by Ruhrchemie by reducing samples for 3, 5, 10, 15, 30 minutes at 400°C. with 300 litres/h. of gas consisting of 75% H₂ and 25% N₂, using a 10 cm. layer of catalyst in a tube of diameter 21 mm., and measuring the fraction of the cobalt reduced to metal. The results, given in Table 10, show that for Co: ThO₂: kieselguhr and Co: ThO₂: MgO: kieselguhr catalysts the reducibility falls to a minimum as the kieselguhr content is increased from 100 to 1,000 parts per 100 parts cobalt.

Table 10.Reducibility of Catalysts

Catalyst Co: ThO ₂ : MgO: Kieselguhr	Time of Reduction, Minutes	Cobalt reduced to metal, %
100 : 15 : - : 100	5	79
200		73
600		47
1,000		28
2,000		36
100 : 5 : 10 : 200	15	78
600		70
1,000		25
2,000		33
100 : - : 15 : 100	15	64
200		64
600		63
1,000		62
2,000		53

For Co: MgO: kieselguhr catalysts, however, the reducibility is unchanged over this range of kieselguhr contents. For catalysts with a constant amount of kieselguhr the reducibility varies with the promoter, increasing in the order MgO, MgO-ThO₂, ThO₂. In

In general, the reducibility is very sensitive to the presence of impurities, particularly nickel and copper, which facilitate reduction. For this reason very pure kieselguhr give catalysts which are very difficult to reduce.

The reducibility was also investigated by reducing the catalyst for a fixed time (exact period not stated, probably 1 hour) at a series of different temperatures and measuring the fraction of the cobalt reduced. Thus for the Co:100: ThO₂ 5: MgO 10: kieselguhr 200 catalyst, 15% was reduced at 300°, 45% at 325° and 75% at 350°C. Of a very large number of preparations tested, the most readily reducible was Co 100: ThO₂ 15: asbestos 200, which was 50% reduced at 250°C., and the most difficult was Co 100: MgO 15: MgO 75 (magnesia as promoter precipitated on to magnesia as a carrier) which was only 24% reduced at 450°C.

Catalysts that are difficult to reduce usually have a long life, but in comparing activities it must be remembered that initially a catalyst with low reducibility and hence low degree of reduction will appear less active than one which is more completely reduced. It may take a long time, 10 days or more, for the degree of reduction of a catalyst of low reducibility to increase up to the equilibrium value.

Hydrogen Revivification.

This is done on the large scale with a gas rate of 1,000 cu.m./reactor/h. and is continued for 7 - 10 hours at a temperature either 5° higher than the last synthesis temperature (Ruhrchemie) or always at 200°C. (Essener Steinkohle). Ruhrchemie found that the reaction is inhibited by pressure and also by small amounts of carbon monoxide, and hence recommended that pure hydrogen should be used. Rheinpreussen, however, say that a little carbon monoxide has no bad effect and Essener Steinkohle only use 86% hydrogen.

This treatment does not remove as much wax from the catalyst as is removed by extraction with a suitable solvent. The organic material not removed, called the 'Restbeladung' can be recovered by extraction in the laboratory with benzene. It is a dark brown solid, of m.p. ca. 90°C., which smells as if it contained oxygen compounds.

If the amount of Restbeladung present in a catalyst is plotted against the time of synthesis, the curve is convex to the time axis, whereas if the same curve is plotted for the total amount of wax, it is concave. The main factors which affect the amount of Restbeladung are the nature of the kieselguhr and the composition of the catalyst.

The products obtained by this hydrogen treatment depend, as far as their composition is concerned, on the amount of hydrogen used, and for the normal large scale treatment 50 - 60% consists of methane and the rest boils below 200°C. and is completely saturated. It is thought that the first methane produced comes from branched chain wax, and this is in accord with the conclusions of Brabag about the presence of branched chain hydrocarbons in catalyst wax.

There is no evidence that the revivification produced by hydrogen is due to any cause other than the removal of wax. Brabag say that the improvement in activity is short lived, since less wax is removed than in the case of solvent extraction.

Essener Steinkohle add the hydrogen that has been used for this treatment, and which, therefore, contains methane, to the synthesis gas going to Stage II to increase its H_2/CO ratio. Or if there is a shortage of coke-oven gas it may be added to the synthesis gas for Stage I.

Solvent Extraction.

The original method recommended by Ruhrchemie was to fill the entire reactor with Diesel oil and leave it for 24 hours. This, however, allowed dust to settle and cause blockages, and in bad cases it took weeks of work to empty the reactor. Brabag tried to overcome this trouble by distilling the Diesel oil directly into the reactor and subsequently they introduced the technique of spraying it in which is now generally used as the normal method. Essener Steinkohle use a continuous extraction method in which the oil is distilled into the top of the reactor, the solution of wax flows out at the bottom into a small portable still, where it is distilled and the oil vapour re-introduced into the top of the reactor. The temperature is kept at 100°C. and the process continued till no more wax is removed. For a block of four reactors about 60 cu.m. oil are in circulation. They use oil of boiling range 80 -

200°C. but most of it boils from 180 - 200°C. Brabag stress the point that the oil used for the extraction must be purified before use or the catalyst is liable to be damaged. For this reason the same oil is used over and over again as the repeated distillations purify it and keep it in a suitable degree of purity.

Extraction of catalysts with solvent on a large scale usually reduces the wax content to 1 - 2%, and is, therefore, more efficient than treatment with hydrogen, which leaves 2 - 5%. But in spite of this, it is generally agreed that the best revivification is achieved and the wax and other materials removed most rapidly by extracting the catalyst with solvent and then treating it with hydrogen. Although solvent alone removes more wax than hydrogen alone, Essener Steinkohle regarded solvent extraction as the milder treatment and used this alone during the first part of the catalyst life. Only when it ceased to respond to such treatment was the more vigorous combined treatment used. Details of this are given in Table 15, in which connexion it should be stated that the normal practice was to follow the extraction by the hydrogen treatment immediately, although in the example shown in Table 15 two days by synthesis was done between the two treatments to see how far the activity was restored by the solvent alone. Ruhrchemie stated that the only reason they did not follow solvent extraction by treatment with hydrogen was their shortage of hydrogen.

Catalyst Wax.

Using the standard large-scale catalyst, from 2 to 2½ t. wax was recovered by each solvent extraction from one reactor. It was realized, however, that the amount of wax produced depends on the catalyst composition, and Ruhrchemie investigated this as follows. The first period of synthesis, see Table 11, was done for so many days at a given temperature, and the catalyst then treated with hydrogen. The conditions are not given, but in other experiments of a similar type carried out at the same time, the hydrogen treatment was done at 5 - 7°C. above synthesis temperature, using a mixture of 75% hydrogen and 25% nitrogen. The products obtained gave the difference between the total wax in the catalyst and the Restbeladung. This latter was determined by extraction with benzene. Another sample of the catalyst was taken and the above treatment repeated up to and including the hydrogen treatment. Synthesis was then

restarted for a second period, at the end of which both acetaldehyde and total wax were determined as before. By proceeding in this way, the results given in Table 11 were built up.

The effect of the nature of the kieselguhr was first examined using two catalysts, both of the composition Co 100: ThO₂ 18: kieselguhr 200, but one made with kieselguhr 120 and the other with kieselguhr S.11. The data in Table 11 show that the Restbeladung and the total wax are dependent on the nature of the kieselguhr.

Table 11

Effect of the Kieselguhr on the Formation of Catalyst Wax

Period	Temperature, °C.	Time, hours	Weight of wax, g.			
			Kieselguhr 120		Kieselguhr S.11	
			Total	Restbeladung	Total	Restbeladung
1	185	1,200	22.1	12.0	21.5	7.0
2	188	650	21.5	15.0	18.0	10.0
3	190	410	20.4	16.2	16.5	10.8
4	192	400	21.5	17.0	15.7	10.2
5	192	220	18.1	15.6	12.5	9.6
6	193	250	18.7	15.8	13.4	11.0
7	194	310	17.6	15.4	13.8	12.0
8	194	250	19.0	17.0	15.0	13.5

The effect of the promoters was then investigated, and the results given in Table 12 show very clearly that thorium increases the formation of catalyst wax and magnesia reduces it to a very small amount. Three catalysts were used, the thorium catalyst of composition Co 100: ThO₂ 15: kieselguhr 200, the thorium-magnesia catalyst Co 100: ThO₂ 5: MgO 10: kieselguhr 200, and the magnesia catalyst Co 100: MgO 15: kieselguhr 200. In all three cases kieselguhr was used and synthesis took at 185°C.

Table 12.Effect of Promoters on the Formation of Catalyst Wax

Period	Time, hours	Weight of Wax/4 g.Co, g.					
		Thoria		Thoria-magnesia		Magnesia	
		Total	Rest-bela-dung	Total	Rest-bela-dung	Total	Rest-bela-dung
1	1,550	26.0	22.0	19.8	8.4	9.0	0.4
2	300	26.6	20.6	12.6	5.6	2.4	0.4
3	400	25.2	21.6	11.6	6.0	2.6	0.8

Brabag have found that the hard wax first formed on the catalyst decomposes as synthesis proceeds and gives heavy oil or soft wax. Thus if a catalyst that has been used for synthesis at 160°C. for 100 hours is extracted, it gives a very hard wax, m.p. ca. 90°C. A catalyst that has been run for 100 hours at 185°C. gives a soft wax on extraction, but by continuing the synthesis till 2,000 hours, high melting wax is again found on the catalyst.

A wax formed on the catalyst at any temperature changes its composition if the synthesis temperature is altered.

In addition to the wax, Ruhrchemie say that if a used catalyst which has been exhaustively extracted with benzene is then boiled with caustic soda solution, sodium salts of fatty acids - mainly of propionic acid - are obtained. They think that these acids were present in the used catalyst as sodium salts and not as cobalt salts.

In medium pressure synthesis cobalt salts of fatty acids are produced and appear in the wax, where they give rise to discoloration. Ruhrchemie have a patent for removing these acids as they are formed, before they react further to give cobalt salts, by continuous extraction with Diesel oil, which is sprayed over the catalyst during synthesis. They do not recommend this process for the large plant as it has no other good effects; it does not

increase the yield of products or the life of the catalyst and produces no great cooling effect.

The K.W.I. consider that these fatty acids are one of the causes of catalyst deterioration.

Dry Regeneration.

At the end of some six to eight months synthesis the catalyst can no longer be revived by solvent or hydrogen treatment in the ways described, as these processes no longer remove the wax and other organic material which has collected on the catalyst, and naturally, they cannot remove the more active catalyst poisons such as free carbon or sulphur. Ruhrchemie found that a catalyst in such a state could be largely reactivated by their so-called dry regeneration, which was done with 75% hydrogen, 25% nitrogen at a high gas rate, as in reduction. The temperature is kept at 200°C. for 1.5 hours, then increased steadily to 450°C. during the course of 2 hours and kept at that temperature for a further 2 hours.

The effectiveness of this treatment can be seen from the following example. A catalyst of composition Co 100: ThO₂ 5: MgO 10: kieselguhr 200, which had been used for synthesis for 500 hours at 185°C., contained 320 g. deposit/100 g. cobalt. On dry regeneration 314 g. of the deposit were removed and recovered, as follows:-

181.0 g.	CH ₄	and higher hydrocarbons
2.6 "	CO ₂	
1.4 "	CO	
130.0 "	Wax	
	"	
<u>314.0</u>	"	

Before dry regeneration 50% of the cobalt was present as metal, after regeneration 75 - 80%.

The removal of sulphur by this treatment is shown by the data in Table 13.

Table 13.

Removal of Sulphur by Dry Regeneration

Sulphur in Catalyst g./ 100 g. Co		Sulphur Removed %
Before	After	
12.36 0,005	2.74 0,001	78 80

The removal of carbon was also proved by depositing 35 g. C/100 g. Co on a catalyst by the decomposition of carbon monoxide. The catalyst was thereby rendered inactive. Dry regeneration removed 75% of the carbon as methane and restored the activity. Ruhrchemie consider that carbon is slowly formed on the catalyst during normal synthesis and quote experiments on a Co 100 : ThO₂ 5 : MgCO₃ 135 catalyst to support this. After synthesis, the catalyst was extracted with solvent and then dissolved completely in acids and the residue collected. This residue consisted of carbon mixed with wax, and the amount of free carbon was estimated from an elementary analysis. After 360 hours synthesis at 185°C., 0.30 g. carbon per 100 g. cobalt was found, and after 370 hours at 200°C., 1.72 g. The K.W.I. were careful to point out that although carbon formed on the catalyst by decomposition of carbon monoxide is a powerful poison, ordinary carbon mixed with the catalyst is not.

Although it is realised, in a general way, that dry regeneration can only be used for catalysts which are resistant to sintering, i.e. for those which are difficult to reduce, there is little agreement about the importance of sintering as a factor causing loss of catalytic activity. Thus Ruhrchemie say, on the one hand, that their so-called hard reduction, which is carried out at 400°C. for 2 hours, will show up ease of sintering. But, on the other, they say that sintering does not occur appreciably below 450°C. The K.W.I. does not think that sintering plays any part in the normal loss of catalytic activity during synthesis.

It should be emphasised that Ruhrchemie have not yet tried dry regeneration on the full scale for two reasons, Firstly, shortage of hydrogen, because, unlike reductions, dry regeneration cannot be done with recirculation of the hydrogen on account of the methane formed. Secondly, because after dry regeneration the catalyst needs screening in an atmosphere of carbon dioxide and no arrangements for doing this were available.

They have not tried it, even in the laboratory, for catalysts which have been used at medium pressures.

Regeneration by Oxidation

Ruhrchemie found one case, accidentally, where oxidation followed by re-reduction was very effective in regenerating the catalyst. Further investigation showed, however, that the method is in general a bad one, the reason being that at the high temperatures reached during the oxidation, the cobalt oxide goes over to a form which is difficult to reduce successfully.