

E. Treatment with Hydrogen Before and During Synthesis.

1. Pretreating with Hydrogen

The normal iron catalyst was pretreated with 6 li of hydrogen/h at 0.1 atm and 325°C for 2 1/2 hours instead of the forming with carbon monoxide. The synthesis was next changed over to carbon monoxide-rich synthesis gas at 15 atm pressure and 235°C. An end gas analysis taken after 1 1/4 hours show the contraction of 2 - 3 percent and after 3 1/4 hours a 4 percent contraction. The behavior of the catalysts showed the effects of pretreatment. The catalyst however, when taken out of the reaction chamber was slightly pyrophoric and ferromagnetic. In a parallel test in which the catalyst was pretreated with carbon monoxide instead of hydrogen, with other conditions remaining the same, the contraction of 54 percent was obtained immediately after starting synthesis. In a subsequent experiment a catalyst of lower activity was used to see whether a pretreatment with hydrogen before forming would cause any improvement. For this purpose the catalyst was first treated for six hours with 8 li of hydrogen/h at 0.1 atm and 325°C and then for four hours with 4 li carbon monoxide/h, at 0.1 atm and 325°C, and was finally used with a high-carbon monoxide synthesis gas at 15 atm. On the second day the contraction at 234°C amounted to 42 percent, on the sixth day at 236°C it was 45 percent, on the eighth day 47 percent at 238°C and 47 percent on the tenth day at 238°C. Parallel tests made with a similar catalyst without pretreatment with hydrogen gave 42 percent at 234°C on the second day, and 46 percent on the eighth day at 235°C. The hydrogen treatment had therefore no effect upon the conversion.

2. Hydrogen Treatment Between Forming and Synthesis

The forming was first done for 2 1/2 hours at 325°C and 0.1 atm by passing 40 li of carbon monoxide over the catalyst. It was next treated for seventeen hours with 6 li of hydrogen/h at 325°C and atmospheric pressure. It was next tested with carbon monoxide-rich synthesis gas at 15 atm pressure and the activity found at 210°C, right after changing over, the conversion amounted to 42 percent, and 43 percent after one day. In a parallel test without

hydrogen treatment the contraction after one day was 42 percent. The treatment with hydrogen had therefore no effect upon the activity of the catalysts. (The results were surprising in that one was justified to expect that the carbides formed during forming and during synthesis would be destroyed by treatment with hydrogen).

3. Treatment with Hydrogen During the Synthesis

A catalyst that had to be operated at a temperature several degrees higher to produce its maximum activity was started at 235°C under normal conditions (15 atm 5 li/CO-rich gas/h). The contraction on the second day was 52 percent (see figure 10), 50 percent after two days and 47 percent contraction after three days. The broken line figure 10 representing a parallel test shows that a contraction of 40 percent was reached after one week of operation at 235°C. However, after three days the catalyst was subjected to a hydrogen treatment (15 hours, 8 li/h, 1 atm, 325°C). The contraction rose to 55 percent after this hydrogen treatment during the synthesis that followed it. It dropped after that but remained 51 percent up to the twelfth day. The catalyst was then again treated with hydrogen (under the same conditions) the contraction rose then to 57 percent and dropped to 50 percent on the nineteenth day. After a third treatment with hydrogen the contraction rose at first to 55 percent, dropped to 51 percent after three days and was 52 percent after four days. The contraction of this run at 235°C remained at values of 50 - 53 percent for two months.

Figure 10 shows that a hydrogen treatment introduced during the synthesis resulted in increasing the activity of the iron catalysts. This was particularly large during the first hours after the hydrogen treatment, but resulted also in some lasting improvement in the catalyst. In the activity peaks obtained immediately after hydrogen treatment, the proportion of carbon monoxide to hydrogen consumed was no different than obtained in the normal courses of synthesis with a contraction of 50 - 52 percent. In both cases the carbon monoxide and hydrogen were consumed in a proportion of 1.67 to 1.70 : 1. The peaks would therefore not represent any carbon deposition upon the catalyst.

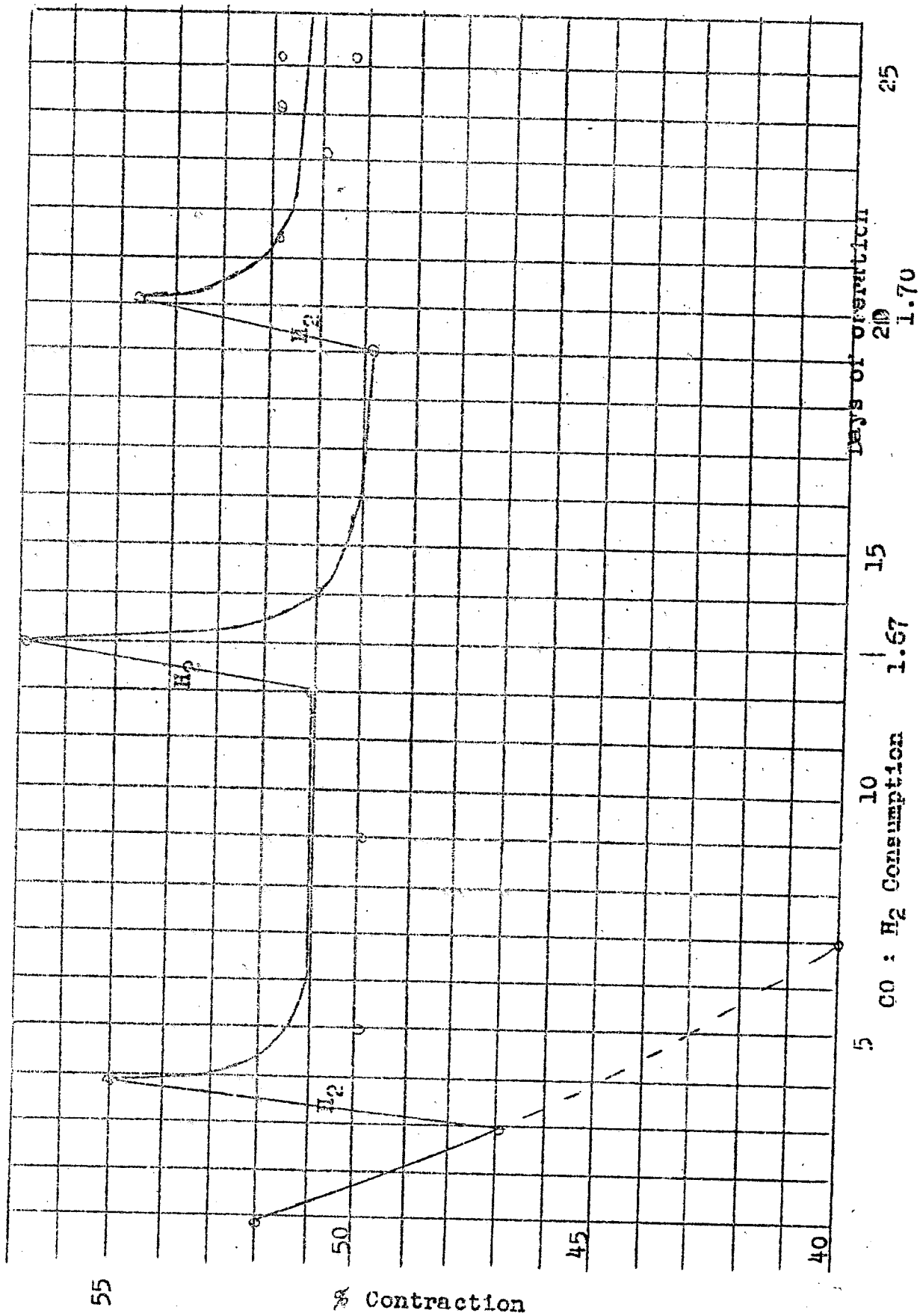


Fig. 10, Effect of treatment with hydrogen upon synthesis

Iron catalysts already used for a long time or which showed a marked drop in activity showed no reactivation after such a hydrogen treatment. Nor can such an improvement be obtained by a later forming with carbon monoxide. The increase in the life of some of the catalysts resulting from the hydrogen treatment must be done prior to the drop of the contraction to below 45 - 50 percent.

F. Catalysts Produced from Ferrous Salts.

It has already been mentioned in the description of the preparation of the catalyst that a voluminous brown powder was obtained when the iron catalysts were made from ferrous salts, while the catalysts made from ferric salts were black and hard and with a vitreous fracture. The two types of catalysts differ therefore outwardly very greatly in their appearance.

When operations with "ferrous catalysts" were started without forming (CO-rich gas, 15 atm), the results were as unfavorable as has already been described with other catalysts. (e.g. a 8 percent contraction was produced on the first day with 244°C and a 45 percent contraction on the ninth day at 265°C. Under these conditions the "ferric catalysts" reached its complete conversion of 50 percent at 280 - 290°C.

Forming with the mischgas at 1 atm and 254°C produced 43 percent contraction at 15 atm and 245°C (CO-rich gas), 44 percent on the tenth day at 255°C and 47 percent contraction at 265°C on the tenth day.

Copper-free iron catalysts made from ferrous chloride or nitrate, formed with carbon monoxide at 0.1 atm and 325°C and then put in operation at 15 atm with CO-rich gas, had a great initial activity which, however, began to drop after one to two days.

Table 23 showed results in these three tests. The contraction of the first test dropped at 235°C on the third day from 57 to 34 percent. In the second test after finding a 56 percent contraction on the first day at temperatures lowered to prevent any possible damage to the catalysts through too high activity. At lower temperatures the contraction dropped however, again. In the third test the catalysts prepared from ferrous nitrate behaved similarly.

Table 23

Test with "Ferrous Catalysts"

Catalysts Prepared from:	FeCl ₂		FeCl ₂		Fe(NO ₃) ₂	
	Temp °C	Contr %	Temp °C	Contr %	Temp °C	Contr %
1	235	57	235	56	235	56
2	235	57	225	56	235	57
3	235	34	225	49	235	40
4	235	30	215	38		
5			225	35		
6			225	29		

The optimum operating conditions given for the normal catalysts (prepared from solutions of ferric salts) show that the "ferrous catalysts" performed considerably poorer.

In the tests on table 12, iron-copper catalysts made from FeCl₂ - copper chloride were used. They were formed with mischgas at atmospheric pressures. The table states that these "ferrous catalysts" caused a complete conversion for several months in accordance with the conditions of their forming, but only at temperatures of 260°C and higher.

G. The Effect of Additions of Copper

Franz Fischer, Ackermann, and Meyer 17/, have shown that the activity of copper-containing iron catalysts was superior to the copper-free catalysts at atmospheric pressure. Table 24 shows the best results obtained with the two types of catalysts at atmospheric pressure. The reaction temperature was 230 - 235°C, with 4 l1 mischgas/h and per 10 g of Fe during the conversion.

The Effect of Copper Addition upon the Synthesis
at Normal Pressure.

Days of Synthesis	Fe : Cu = 5 : 1 2 days		Fe(no Cu) 4 - 7 days	
	Contr. %	Liquid products g/ncbm	Contr. %	Liquid product g/ncbm
1	30	56	32	55
5	30	56	31	50
10	30	55	30	48
20	30	56	27	38
30	29	50	26	34
40	27	46		

The copper-containing catalysts requires less time to produce the maximum contraction of around 30 percent. The maximum yield was about the same at the beginning of synthesis in both cases, but the copper-containing catalysts remained for several weeks equally active, while the copper-free catalysts lost their activity in a few days.

When synthesis was correctly conducted at a pressure of 15 atm (without previous forming at lower pressures), catalysts without as well as with copper additions (5Fe : 1 Cu) produced a contraction of 40 - 44 percent only at 260 - 270°C. Without addition of copper a contraction of 50 percent was reached at 280 - 290°C and kept there for several months, while the activity of the copper-containing catalysts fell off rapidly at these temperatures.

Table 25 shows two pairs of tests with catalysts made from ferric salt solutions and formed with carbon monoxide at 0.1 atm and 325°C. The synthesis was carried out with CO-rich gas at 15 atm. The results are compared of syntheses at 235 and 225°C with and without copper.

Table 25The Effect of Copper Addition upon the Activity of Iron Catalysts.

Days of operation	235°C		225°C	
	Fe, no Cu	Fe-Cu 5 : 1	Fe, no Cu	Fe-Cu 5 : 1
1	55	54	52	55
2	53	56	-	54
3	53	-	50	50
4	55	50	-	-
5	55	50	45	50
10	54	52		

The tests show that an addition of copper to iron catalysts results in no advantages in middle pressure synthesis after proper forming at 235°C.

H. The Effect of Addition of Kieselguhr

The addition of kieselguhr to cobalt catalysts is outstandingly important for the synthesis of hydrocarbon. Good yields in liquid and solid hydrocarbons can only be obtained with catalysts containing kieselguhr.

With normal pressure synthesis, on the other hand the addition of kieselguhr to iron catalysts resulted in the formation of catalysts invariably lower in activity than when no kieselguhr was used. 50 - 55 g liquid hydrocarbon/cbm were found in a few cases, but the life of these catalysts was only a few days.

Recently tests have been undertaken on middle pressure synthesis with iron catalysts in which kieselguhr was used as a carrier. These tests were intended to show whether a loosening up of the catalysts would improve their stability in the vertical reaction tubes, rather than to improve the iron catalysts in the sense of increasing yields. (see part IV of this work).

Kieselguhr was added at the different stages of the catalysts preparation. The following experiments might be mentioned:

Experiment #1, 4 g kieselguhr were added to 10 g of Fe before the precipitation from the iron solution.

Experiment #2, 4 g kieselguhr/10gFe were added to the sodium hydroxide solution before the precipitation.

Experiment #3, 4 g kieselguhr/10gFe were added to the moist catalysts paste after alkalizing (see part I, preparation of catalysts).

Experiment #4, The possibility of adding dry kieselguhr to a ready catalyst is excluded if a hard grainy catalyst is being prepared.

The results obtained in experiments 1 - 3 are summarized in table 26, experiment 3a was conducted at synthesis temperature of 235°C, 3b at 225°C. The contractions found after different operations time are recorded. In all cases forming was done for 24 hours with 4 li carbon monoxide/10g/h at 0.1 atm and 325°C, and the synthesis then performed with a carbon monoxide-rich gas (3CO : 2H₂) at 15 atm.

Table 26

The Effect of the Addition of Kieselguhr to Catalysts

Days of Operation	Exper #1		Exper #2		Exper #3a		Exper #3b	
	Temp °C	Contr %	Temp °C	Contr %	Temp °C	Contr %	Temp °C	contr. %
1	235	53	234	55	235	54		
2	235	50	234	53	235	54		
3			234	51			225	56
4			234	50			225	56
5			235	49	235	54	225	54
6	234	45	236	50	235	54	225	54
8			235	49	235	56	225	54
9			234	40	235	55	225	50
10					235	54	225	46
20					235	54		
30					235	52		
40					235	52		
50					235	50		
60					235	50		

Table 26 shows that results obtained in experiment 3a are best. In this case kieselguhr had been added after alkalizing. The contraction remained over 50 percent (without reactivation) after two months of operation. At 225°C (experiment 3b) the contraction dropped to below 50 percent after ten days.

Table 27 shows the composition of the reaction gas with a contraction of 53 - 54 percent. Experiment 3a produced the most gaseous hydrocarbons. Catalysts prepared with kieselguhr present during the precipitation which had a chance to become saturated with alkali (experiments 1 and 2) as well as the experiment 3b conducted at 225°C produced considerably less gaseous hydrocarbon. (The normal iron catalysts under analogous conditions produces a reaction gas with 6 - 8 percent saturated gaseous hydrocarbons).

Table 27
Analysis of Reaction Gases of the Kieselguhr Catalysts
with a Contraction of 53 - 54 percent

	CO ₂	Heavy Hydro- carbons	O ₂	CO	H ₂	Hydro- carbons	Carbon Number	N ₂
Test 1	59.1	3.5	0.2	6.3	12.9	4.7	1.8	13.3
Test 2	59.2	4.4	0.1	5.4	11.1	6.1	1.7	12.7
Test 3a	64.8	3.0	0.1	1.3	6.0	11.4	1.9	13.4
Test 3b	55.9	2.6	0.2	8.8	9.9	7.7	2.1	14.2

The analysis of yield in experiment 3a gives 87 g of solid and liquid hydrocarbons and 36 g gasol hydrocarbons /ncbm ideal gas.

The liquid hydrocarbons contained at first 3 percent solid paraffin, 12 percent after four weeks and 14 percent after six weeks. (This catalyst was alkalized with 1 percent potassium carbonate. The paraffin formation is therefore considerably less than with the clear kieselguhr-free iron catalysts).

The products obtained were colorless and their composition is described elsewhere.

A catalyst prepared in accordance with experiment 3 was used in filling a vertical apparatus with 18 tubes (18 catalysts fillings for 10 g of Fe). The forming with carbon monoxide preceded in the usual

way at 0.1 atm and 325°C and operations were then started with carbon monoxide-rich gas at 15 atm and 225°C. The contraction dropped in the course of six days from 54 to 50 percent, the catalysts was then reactivated at the same temperature with hydrogen. On the eighth day the contraction was 52 percent, on the tenth day 47 percent. After a second treatment with hydrogen at 230°C the operations were conducted at 232°C. The contraction again dropped to 48 percent on the seventeenth day. After a repeated hydrogen treatment the test was continued for one week at 236°C etc. (see figure 11).

In comparison with corresponding tests in horizontal or weakly inclined tubes showed that the experiment 3 in table 26 in a vertical apparatus proceeded less uniformly. Nevertheless with repeated hydrogen treatment a contraction of around 50 percent could be maintained. (The apparatus is discussed in greater detail in part IV).