Physico-Chemical Investigations on Catalytic Mechanism. IV.[1] On the Fischer-Tropsch Synthesis of Hydrocarbons. (Experimental Series I[1]).

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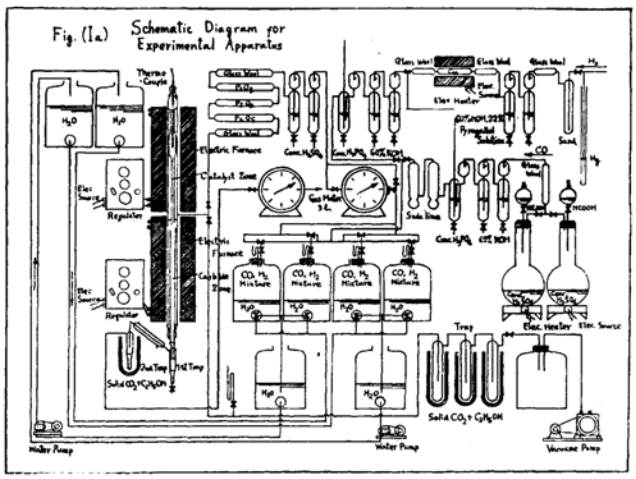
We have already published[2] our newly proposed mechanism for the Fischer- Tropsch synthesis. In this paper we shall describe experimental aspects of this investigation, and some considerations on the experimental results will be made to substantiate our theory.

Experimental Apparatus[3]. The experimental apparatus is as shown in Fig. 1 a and 1 b. The main feature of the reaction vessel is its double walls. Owing to them, the gas mixture ($CO+2H_2$), led in, can be heated beore entering the catalyst zone into which the thermocouple well is thoroughly inserted to measure accurately even a slight variation of the temperature at which the reaction is occurring.



The double walled reaction vessel, 70 cm in length (the catalyst zone, about 60 cm.), is made of terex glass, and the diameter of the inner tube

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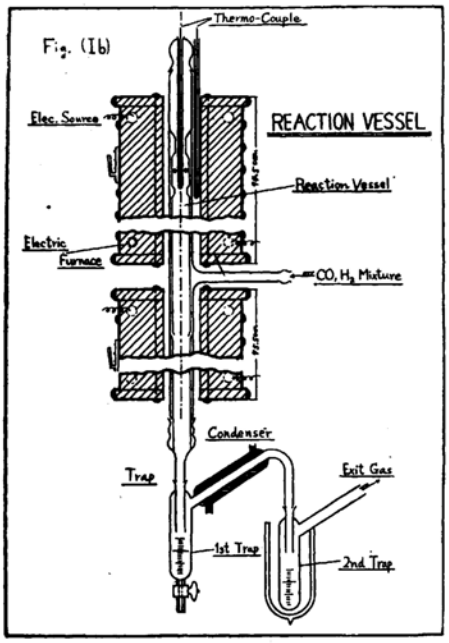
(1) Report III in this series of Papers was published in *J. Soc. Chem. Ind. Japan*, **45** (1942), 313.

(2) (a) S. Hamai, *Jour. Chem. Soc. Japan*, **62** (1941), 516.
(b) S. Hamai, This Bulletin, **16** (1941), 213.

(3) The experimental apparatus shown here was specially designed as to have two reaction zones with the purpose of studying the two staged reaction with or without catalyst, and the combination reaction.—The detailed report for this series of investigations is to be given in our report subsequently published elsewhere.



is 1.4 cm and that of the outer tube, about 2.7 cm. A brief sketch is shown in Fig. 1 b. The temperatures of the electric furnaces are controlled by means of accurate regulators of potentiometric type. The catalysts which we have used are of Co type, of Fe and Co + Fe types with various promoters and kieselguhr. In this series of experiments we mainly employed the catalyst XII_{16}–I (Co type), which was prepared by the precipitation method from cobalt nitrate with potassium-carbonate, mixed adequately with various promoters and kieselguhrs; then thus prepared catalyst was made into tablet forms. The catalyst was reduced with hydrogen at 350°–375°C. just before we proceeded with the synthesis; so that there was not even a slight chance of air being in contact with the catalyst before starting the experiment. Furthermore, no heat treatment was proceeded prior to H_2 reduction.

Preparations of Catalyst. For the preparation of the catalyst, the materials used were:

$Co(NO_3)\cdot 6H_2O$	Extra pure, (Kojima)
$Ce(NO_3)_3\cdot 6H_2O$	,, (Katayama)
$Th(NO_3)_4\cdot 4H_2\cdot O$	,, (Kojima)
$K_2O\cdot 5B_2O_3\cdot 8H_2O$	Guaranteed reagent, (Kojima)
K_2CO_3	Extra pure, (Kojima)
Kieselguhr	

Kieselguhr was purified by treating with HCl, HNO_3 and by heating at 500°C for 5~10 hrs. while the air was streamed through it, and these processes were repeated twice at least. Before the purification, its appearance was yellow, but when it was purified as such as mentioned above, it looked absolutely white.

These materials were taken in the calculated amount for the desired catalyst composition and then precipitated by 2N K_2CO_3 solution into carbonates, washed thoroughly with hot distilled water at least ten times until they became entirely free from the adsorbed nitrate ion and other possible impurities. Then they were dried at 100°–110°C. and finally made into small sized tablet forms by the tablet machine.

Preparations of Gases involved in the Reaction. *Hydrogen.* Hydrogen used was of commercial cylinder (electrolytic hydrogen) and was purified very carefully, as shown in the schematic flow diagram Fig. 1 a: firstly, by passing through two tubes of alkaline pyrogallol solution

(60% alkaline solution, 22% pyrogallol solution)[4], then by heating in the tube which contained Cu gauze at 400°–500°C, and further through H_3PO_4, two tubes of concentrated H_2SO_4 and three tubes of P_2O_5.

Carbon Monoxide.[5] Carbon monoxide was prepared by dropping air free formic-acid into concentrated sulfuric acid at 120°–150°C, as shown in the diagram, and passed over soda lime, H_2SO_4 and then P_2O_5.

Both hydrogen and carbon monoxide thus prepared were collected in the gas reservoir in an appropriate proportion so that we were able to pass these gas mixtures through the catalyst zone with a definite rate of flow at will.

Experimental Procedure. The catalyst was firstly reduced by streaming H_2 at some such temperatures as 350°–375°C at a definite rate of flow, just before we proceeded the reaction, at least for 5–10 hrs. When the catalyst zone was well ready for a run, the H_2–CO mixture (2:1) was passed through this catalyst zone at 200°C with a definite rate of flow (4–8 liters/hr.), and the gas contraction percentage was recorded from time to time by means of the readings in the gas meters installed as shown in our diagram. The amount of the catalyst used was 4 g. on the basis of the weight of Co.

The reaction products were collected in two separate portions, namely, in the first trap at which the vapor is condensed at room temperature, and with the water condenser and in the second trap with the solid CO_2 –C_2H_5OH mixture. The reaction products thus obtained were later subjected to the determinations of physico- chemical constants such as refractive index, specific gravity, apparent molecular weight and elementary analysis, and if the amount was sufficient, the boiling points were also determined. The effluent gas was subjected to gas analysis, using a modified form of Orsat-gas-analysis—apparatus, to determine their constituents.

Experimental Results. Some of the experimental results are tabulated as follows:

Table 1.

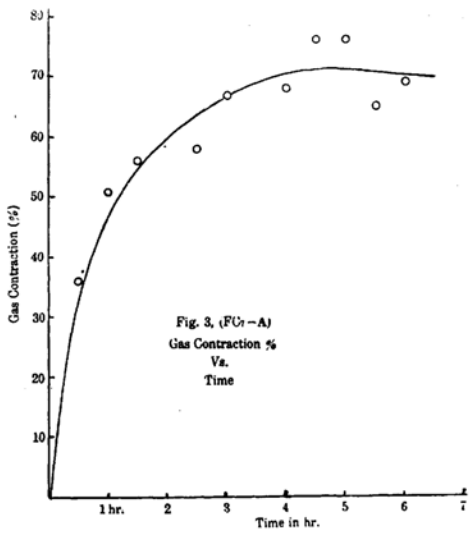
Catalyst[6]	XII_{16}–I			
	Co+15% CeO_2+15% ThO_2+10% B_2O_3+100% Kieselguhr			
Pretreatment	No heat treatment prior to H_2 reduction.			
	H_2 reduction at 350°C for 10 hrs.			
Exp. No.	FC_7-A	FC_7-B	FC_7-C	FC_7-D
Reaction Temperature (°C)	200	200	200	200
Rate of Flow (l/hr.)	4	4	4	4
Space Velocity	242	242	242	242
Average Gas Contraction (%)...	60	61.7	72.8	60.6
Oil Yield c.c./M^3 (c.c.)	28·	111.3	125.4	125

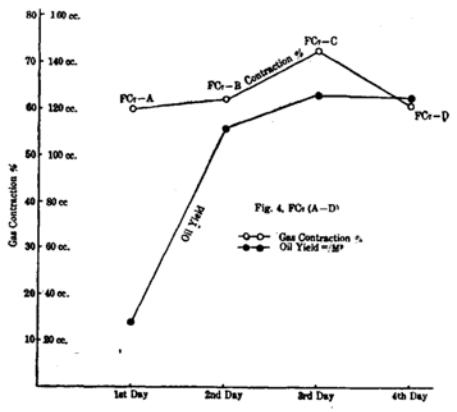
(4) Treadwell and Hall, "Analytic Chemistry," Vol. II, P. 653, 1930.
(5) Farkas and Melville, "Experimental Methods in Gas Reactions" P. 161, 1939.
(6) This catalyst was shown to be capable of yielding (171.7 c.c./M^3) (in F_{49}–F).

Table 2. Gas Analysis Data.

Exp. No.	FC_7-A	FC_7-B	FC_7-C	FC_7-D
CO_2	15.9	9.8	6.8	5.0
C_2H_2	0.0	0.1	0.4	0.0
C_2H_4	0.0	0.0	0.0	0.2
C_nH_{2n}	0.2	0.1	1.6	1.2
O_2	0.2	0.4	0.3	0.6
CO	11.1	24.9	21.8	51.1
H_2	15.5	20.4	42.3	20.8
CH_4(7)	34.3	18.7	16.2	14.6
C_2H_6	0.0	0.0	1.1	0.6
N_2	20.8	24.6	9.5	6.0

As seen in Fig. 3, from the initial stage of the experiment, the gas contraction percentage gradually increases as far as to its contraction percentage for the presumably normalized reaction for which the contraction usually observed to be maintained at some such value as, say 60%;(*) and furthermore, as it is noticed in Fig. 4, a steady contraction percentage was maintained as in the series of FC_7-A, FC_7-B, FC_7-C and FC_7-D, and each of which represents the result from the first day to the fourth day of the experiment. In Fig. 4 the relative oil yields as compared with each of the contraction percentage are plotted. This





apparently shows that the contraction percentage is not necessary to be parallel with the oil yield unless the reaction is normalized as such that the side reactions other than oil forming reactions are to be inhibited as time proceeds, as already pointed out in our previous paper(1); i.e., in the initial stage of the experiment CH_4 formation predominates and it

(7) CH_4 formation tends to be zero as time proceeds.
(*) It is unnecessary to be 60% always.

in turn always cuts down the oil formation. Once the catalyst is normalized, a steady contraction percentage is maintained and a good deal of oil formation is observed.

Durability of the Catalyst.[8] Durability of the catalyst is of paramount importance, as well as its oil forming activity. We shall now demonstrate that the catalyst we used here is well qualified for this purpose. The catalyst XII_{16}–I used in the series of FC_7 has been continuously used in FC_8(A–E), FC_9(A–C), FC_{10}(A–C) and FC_{11} (A–N).

Table 3.

Exp. No.	Gas Contraction (%)	Oil Yield c.c./M³
FC_7–A	60	28 cc.
FC_7–B	61.7	111.3 cc.
FC_7–C	72.8	125.4 cc.
FC_7–D	60.6	125 cc.
FC_8–(A–E)[9] .	Ave. 60	149 cc.
FC_9–(A–C)[9] .	Ave. 56.2	154 cc.
FC_{10}–(A–C)[9].	Ave. 58	123 cc.
FC_{11}–(A–N) ..	59	103 cc.

As seen in Table 3, the contraction percentage are maintained practically about 60%, and the oil yields, however, are fluctuated; the catalyst was shown to be still in a usable form.

Reaction Products. The reaction products were collected in two separate portions as already mentioned. Those collected samples were subjected to the determination of their properties. They may be tabulated as follows:

Table 4.

Exp. No.	FC_7(A-D)	
Reaction Temp.	200°C	
Catalyst No.	XII_{16}–I	
Catalyst Comp.	Co+15% CeO_2+15% ThO_2+10% B_2O_3+100% Kieselguhr	
Pretreatment	No heat treatment prior to H_2 reduction.	
	H_2 reduction at 350°C. for 15 hrs.	
Phys. Const.	1st trap oil (heavier)	2nd trap oil (lighter)
$n_D^{25°}$, Ref. Ind.	$1.4197^{25°}$	$1.3780^{25°}$
$d_{4°}^{t}$, Sp. Gr.	$0.7454^{20°}$	$0.6855^{25°}$
Apparent M. W.	158.4	116.4
Elementary analysis		
C %	84.49	84.60
H %	15.42	15.39

(8) (a) F. Fischer and H. Koch, Brenn-Chem., **13** (1932), 61. Co+18% ThO_2 Catalyst was reported to be so durable that it was capable of being active for 1600 hrs., [(103 c.c./M³), 61.5% Gas Contraction]. (b) F. Fischer, Brenn-Chem., **16** (1935), 1.

(9) FC_8, FC_9, and FC_{10} series are not pure Fischer reaction but a combination reaction with carbide about which details will be published later. Here, we just intend to show that the catalyst is still in useful and efficient condition, as shown in the FC_{11} series.

Those results of other series under different conditions will be compared in our subsequent papers.

Some Considerations in Connection with Our Proposed Theory. In connection with our theory we have stated the fact that at the initial stage of the experiment, the methane formation predominates. This is due to the circumstance that the catalyst surface is not in a well arranged form, namely, not favorable for the oil forming activity, when various factors are taken into consideration which may influence the activity of the main reaction of liquid hydrocarbon formation, but they activate more or less the reaction of methane synthesis through

$$CO + 3H_2 \rightleftarrows CH_4 + H_2O .$$

This reaction is well substantiated in our cited series of experiments, i.e., considering the results shown in Fig. 3–4 and Table 1–2, the activity of the catalyst as indicated in contraction percentage gradually builds up until a steady value of about 60% is attained and tends to remain, and, furthermore, from the values of FC_7–B, FC_7–C and FC_7–D, it is quite apparent that the contraction percentage is more or less maintained; and as already pointed out in our previous paper (Fig. II).[2b] CH_4 formation in every set of experiments tends to be zero as time proceeds. All these observations well substantiate our explanations mentioned already.

Summary.

(1) The experimental apparatus and the experimental procedures were described for the investigations on the Fischer—Tropsch reaction with special reference to its catalytic mechanism.

(2) The durability of the catalyst used was discussed in connection with the investigation of catalytic activity as to its liquid hydrocarbons synthesis.

(3) Some properties of the reaction products were tabulated.

(4) Some consideration of CH_4 formation in connection with our proposed mechanism were presented and correlated with the experimental results.

In conclusion, the authors wish to express their thanks to Dr. T. Marusawa, Former Director of the Institute, and Dr. S. Sato, Director of the Institute, for their interests and the permission for this publication; also to their colleagues for their cooperation; and to Mr. I. Fujiwara who has willingly assisted us in this experimental investigation.

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