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

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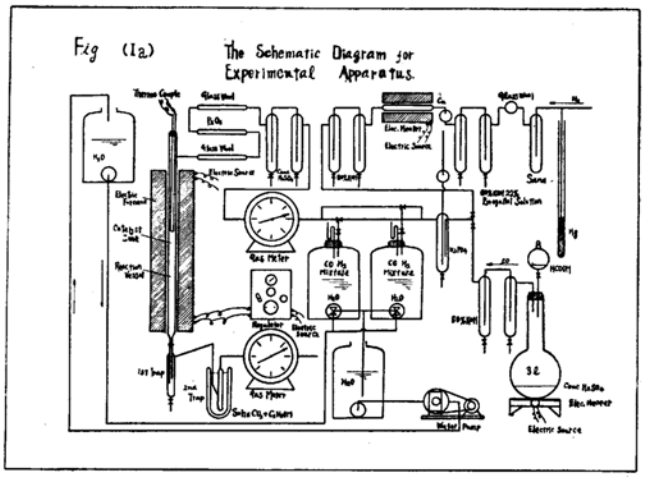
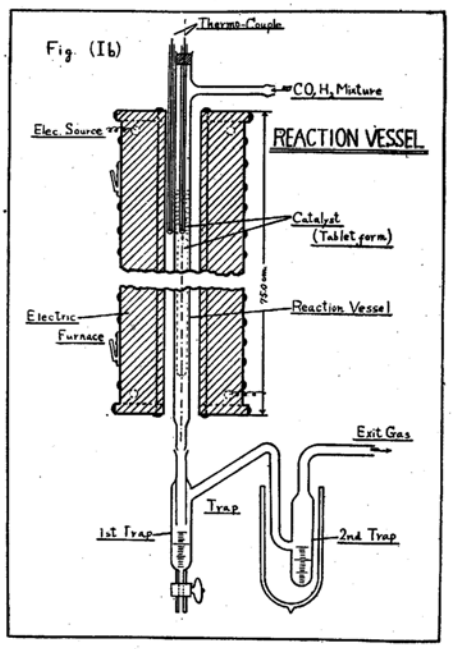
In a previous paper[1] we described the experimental apparatus by which a series of investigations concerning the catalytic mechanism has been studied. In this paper we shall attempt to report some of our further experimental results obtained from similar series of the experiments, made by using other set of apparatus; hereafter, for our convenience we shall call this series II.

Experimental Apparatus. The principal features of the apparatus are practically the same as before, except a few details of the reaction vessel. They are shown in Fig. 1 a and Fig. 1 b.





The main feature of the reaction vessel is, as shown in Fig. 1 b, a tube of all terex glass of which dimension is 1.4 cm. in diameter and

* Most of the results given in this paper were obtained and completed in 1939–1940, but the publication of them has been with-held.

(1) S. Hamai, S. Hayashi, K. Shimamura and H. Igarashi, *Bull. Chem. Soc. Japan*, **17** (1942), 166 (Report IV).

94 cm. in length, and the thermocouple well is well inserted to the tube as far as the middle part of the catalyst zone so as to enable us to record even a slight variation of temperature during a run.

Electric furnace was controlled by means of an accurate regulator of potentiometric type.

Catalyst. The catalysts which we have employed are of Co, of Fe, and of Co–Fe types with various promoters and Kieselguhr.

In this series of experiments we used mainly the catalysts shown in Tables 1–3 (Co type), and they were prepared by the precipitation method from cobalt nitrate with potassium carbonate (2N) with an adequate

Table 1.

Effects of Promoters (CeO_2) on the Gas Contraction Reaction Temperature 200°C.

Exp. No.	Catalyst No.	Catalyst Composition (%) CO+CeO_2+Kieselguhr			Average Gas Contraction (%)
F_{30}(A–G)	XII_1–1	100	5	100	51
F_{31}(A–G)	XII_2–1	100	10	100	54
F_{32}(A–E)	XII_4–1	100	20	100	35
F_{33}(A–D)	XII_5–1	100	30	100	24
F_{36}(A–D)	XII_3–1	100	15	100	56
F_{35}(A–D)	XII_8–1	100	48	100	17

Table 2.

Effects of Promoters (ThO_2) on the Gas Contraction Reaction Temperature 225°C.

Exp. No.	Catalyst No.	Catalyst Composition (%) Co+ThO_2+Kieselguhr			Average Gas Contraction (%)
F_4	1_1–1	100	15	100	40
F_5	1_2–1	100	20	100	70
F_6	1_3–1	100	30	100	70
F_9	1_5–1	100	10	100	6
F_{12}	1_5–1	100	10	100	5
F_{13}	1_6–1	100	48	100	60

Table 3a.

Effect of ThO_2 on the Gas Contraction Reaction Temperature 200°C.

Exp. No.	Catalyst No.	Catalyst Composition (%) Co+CeO_2+ThO_2+Kiesel.				Average Gas Contraction (%)
F_{30}(A–D)	XII_1–1	100	5	—	100	51
F_{37}(A–D)	XII_7–1	100	5	5	100	35
F_{40}(A–G)	XII_{11}–1	100	15	15	100	34
F_{36}(A–D)	XII_3–1	100	15	—	100	56

Table 3b.

Effect of Cu on the Gas Contraction Reaction
Temperature 200°C.

Exp. No.	Catalyst No.	Catalyst Composition (%) Co+CeO_2+Cu+Kiesel.				Average Gas Contraction (%)
F_{30}(A–D)	XII_1–1	100	5	—	100	51
F_{38}(A–H)	XII_6–1	100	5	5	100	25

mixing of various promoters and Kieselguhr as a carrier, and were made into small tablet forms. (For a more detailed description for the preparation of the catalyst, see our report IV[1]).

Preparation of Gases involved in the Reactions. Hydrogen and carbon monoxide were prepared and purified in the same way as already described[1].

Experimental Procedure. As described previously in our report IV, the main features of experimental procedure are the same except that they were carried out in various different conditions.

The reaction products were collected in two separate portions—similar to those of Series I and subjected to the determinations of physicochemical properties.

The effluent gas was analyzed, using a modified form of Orsat Gas Analysis Apparatus for their constituents.

Experimental Results. In the present paper, we concern ourselves especially with different catalysts and their various influences on their activities and attempt to correlate with our theory of Fischer-Tropsch synthesis. Some of the illustrative results are tabulated as follows:

Table 1 and 2 show the influences of CeO_2[2][3] and ThO_2[3][4][5] in various percentages, and the characteristic behaviours of each catalyst are illustrated in Fig. 1 and 2. As seen in these graphs, it is more or less recognizable that the influences of CeO_2 and ThO_2 are not similar but quite distinct; namely in the case of CeO_2, the gas contraction percentage is higher with about 15–10% of this promotor, while if it exceeds 15% such as 20% or over, the gas contraction decreases distinctly. In the case of ThO_2, the gas contraction percentage is higher with about 20–30% of the oxide and below this it is not so favorable with regard to its activity, and one of the interesting points is that the relatively high percentage of ThO_2 content does not influence the activity as much as that of the relatively low one. However, an evenmore interesting point is that if the points of the maximum activity in both cases are traced and the contents of ThO_2 and CeO_2 are expressed respectively in the moral

(2) S. Kodama, *J. Soc. Chem. Ind. Japan*, (Suppl.) **33**, (1930) 202b.
(3) F. Fischer and H. Koch, *Brenn-chem.*, **13** (1932), 61.
(4) S. Tsutsumi, *J. Chem. Soc. Japan*, **59** (1938), 1412.
(5) S. Tsutsumi, *J. Chem. Soc. Japan*, **57** (1936), 685.

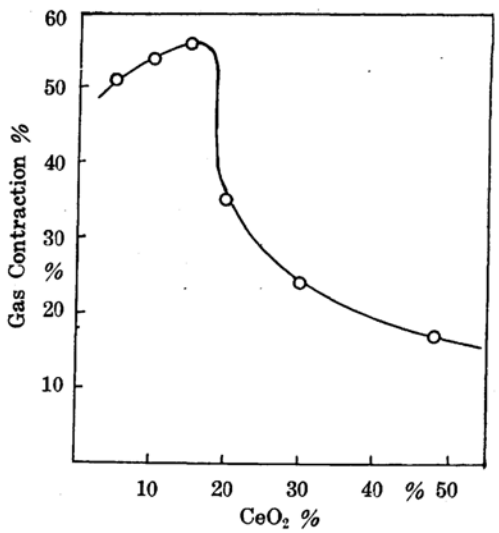


Fig. 1. Effect of CeO_2 % on The Gas Contraction %.
(Relatively High Yield of oil and Less Yield of CH_4)

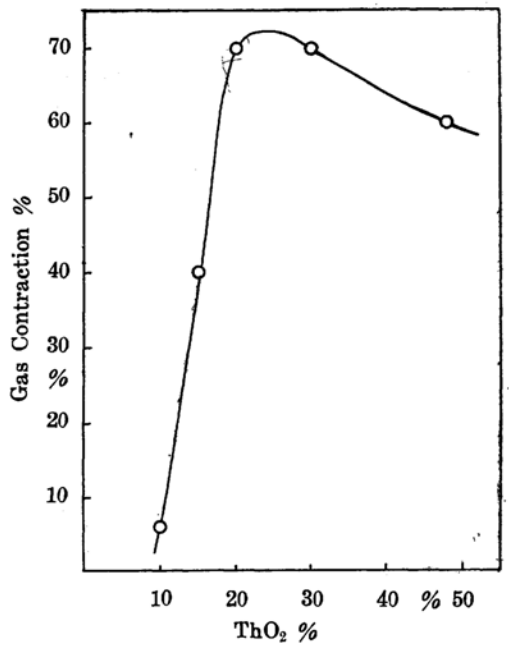


Fig. 2. Effect of ThO_2 on The Gas Contraction %.
(Relatively High yield of CH_4)

ratio(*) instead of the usual weight percentages, strange as they seem, they happen to be about the same, namely $Co:ThO_2=1:0.0513$ (23~25%), $Co:CeO_2=1:0.0513$ (15%), [$Co:ThO_2$, 1:0.0557 (25%)]. These observed facts may be considered to be rather important from the stand point that in connection with the action of promoters, such as ThO_2 or CeO_2, the active centers to which the molecules of the promoters are distributed, are existing in such a manner as they seem to give the definite ratio. The interpretation of these phenomena may be very suggestive in regards to the theory of the promoter action, although such argument should not be put forward too far. At any rate, these facts, may possibly give a consequence fruitful in establishing the theory of promoter action.

Some investigators[3][6] have stated that the activity fell to zero when ThO_2 content was as high as 48%; but in our case the gas contraction percentage has been found to be as high as 60% with the same composition and it showed an activity almost as good as those of 20 and of 30%. These contradictory evidences show clearly that, as far as the catalytic activity is concerned, such a statement as cited in[3][6] does not have so much significance unless such facts are found absolutely reproduceable. This in turn implies that the investigation of catalytic mechanism, especially the catalytic activity, cannot be so easily discussed, even though the ex-

(*) Chemical properties are usually more closely connected with the molal ratio and better to be expressed in terms of molal properties of the system.

(6) S. Tsuneoka, "Synthetic Liquid Fuel" p. 65, (in Japanese).

perimental facts themselves might not be denied. But from these facts not only a clear-cut conclusion cannot be so easily drawn nor should be hastely deduced. Such experimental results themselves only tell a story of one side but not of general. Therefore, we can safely state that such evidence as the gas contraction percentage has true significance only for a definite reproducible condition.

The other interesting point is that, in the series of the catalysts containing CeO_2, a relatively high yield of oil and low yield of CH_4 are found even at the initial stage[7] of the run; while in the case of ThO_2, a relatively high yield of CH_4 and low yield of oil.

Table 3 shows some of the influences of ThO_2 as found on the average gas contraction and the effects of Cu.[8][3] As seen in Table 3, when CeO_2 percentage is relatively low, the addition of ThO_2 is found to lower the activity; while if CeO_2 is as high as 15%, the addition of 15% ThO_2 does not much improve the gas contraction, but it remains practically the same; so that the addition of ThO_2 does not seem to improve the activity as much as expected.

As regards the oil formation, it was found that in F_{36}(A–D), in which the contraction percentage was 56%, the yield of oil was approximately estimated to be 121.3 c.c./M^3.

Some of the typical gas analysis data are tabulated as follows:

Table 4.

Gas Analysis Date

Exp. No.	F_{30}—A	F_{30}—B	F_{30}—C	F_{30}—D	F_{31}—G	F_{32}—E
CO_2	12.8	0.3	0.0	0.5	1.4	0.3
C_2H_2	0.0	0.0	0.0	0.0	0.0	0.0
C_2H_4	0.5	0.2	0.3	0.5	1.4	0.4
C_nH_{2n}	0.0	0.0	0.0	0.0	0.0	0.0
O_2	0.4	0.4	0.3	0.3	0.3	0.4
CO	6.1	31.8	31.5	31.6	29.4	31.5
H_2	39.8	65.2	66.0	65.4	66.1	65.3
CH_4	37.1*	0.0	0.0	0.0	0.0	0.0
C_2H_6	1.4	0.0	0.0	0.0	0.0	0.0
N_2	1.9	2.1	1.9	1.7	1.4	2.1

* Initial Stage.

(7) See: S. Hamai, *Bull. Chem. Soc. Japan*, **16** (1941), 213; Report IV, S. Hamai, S. Hayashi, K. Shimamura and H. Igarashi, *Bull. Chem. Soc. Japan*, **17** (1942), 166; E. F. G. Herington and L. A. Woodward, *Trans. Faraday Soc.*, **35** (1935), 958; *Brenn.-Chem.*, **20** (1939), 319.

(8) (a) F. Fischer, *Brenn.-Chem.*, **11** (1930), 489.
(b) K. Fujimura, *J. Chem. Ind. Japan*, **35** (1932), 532.
(c) S. Tsutsumi, *Report of the Fuel Research Institute, Japan*, **31** (1935).
(d) S. Tsuneoka and Y. Murata, *J. Chem. Ind. Japan*, **41** (1938), 95.
(e) F. Fischer and K. Meyer, *Brenn.-Chem.*, **12** (1931), 225.

Table 4.—(*Continued*)

Gas Analysis Date

Exp. No.	F_{33}—D	F_{35}—D	F_{36}—A	F_{36}—B	F_{36}—C	F_{36}—D
CO_2	0.5	0.2	3.5	0.9	0.3	1.4
C_2H_2	0.0	0.0	0.0	0.0	0.0	0.0
C_2H_4	0.3	0.4	0.9	0.5	0.6	0.7
C_nH_{2n}	0.0	0.0	0.0	0.0	0.0	0.0
O_2	0.2	0.3	0.6	0.3	0.3	0.4
CO	32.5	30.1	16.0	23.3	30.0	30.5
H_2	64.8	67.5	56.8	66.6	67.0	64.9
CH_4	0.0	0.0	19.6*	6.5*	0.0	0.0
C_2H_6	0.0	0.0	0.0	0.0	0.0	0.0
N_2	1.7	1.5	2.6	1.9	1.8	2.1

Table 5.

Gas Analysis Data

Exp. No.	F_4	F_5	F_6	F_9	F_{10}	F_{12}	F_{13}
CO_2	1.0	8.0	0.7	0.2	0.0	0.4	8.5
C_2H_2	0.3	0.3	0.2	0.4	0.0	0.3	0.7
C_2H_4	0.2	0.4	0.2	0.0	0.5	0.2	0.0
C_nH_{2n}	0.5	0.3	0.0	0.0	0.3	0.0	0.0
O_2	0.4	0.3	0.3	0.4	0.4	0.3	0.4
CO	27.1	16.7	26.3	31.7	30.9	30.2	0.4
H_2	68.4	59.0	70.8	65.5	66.3	67.3	46.0
CH_4	0.0	12.8*	0.0	0.0	0.0	0.0	41.2*
C_2H_6	0.0	0.9	0.0	0.0	0.0	0.0	1.1
N_2	2.1	1.3	1.5	1.7	1.7	1.3	1.6

* Initial Stage.

As seen in these tables, CH_4 formation was observed at the initial stage[7] (F_{30}–A), F_{36}(A–B). In the case of F_{13} where ThO_2 content was 48%, the relatively high gas contraction percentage might be due to this abnormally high yield of CH_4.

As regards the influence of Cu on the activity of F_{30}(A–D) and F_{38}(A–H), it might be stated that, as far as these series of experiments are concerned, the addition of Cu seemed to lower the activity as evidenced by the average gas contraction. However, we must be cautious about drawing a general conclusion.

Thus far, we have shown some of typical results which indicate the various influences on the catalytic activity as caused by various amounts of promoters such as CeO_2, ThO_2 and Cu, along with the gas analysis data.

In Table 6 we have shown some of the physical and chemical properties of 1st and 2nd trap oils for the respective experiments.

Table 6.

Exp. No.	Reaction Temp. (°C)	Catalyst No.	Catalyst Comp. Co+ThO_2+Kieselguhr	Pretreatment hrs. °C	Physico-Chem. Properties: Ref. Ind.	Sp. Gr.	App. M. W.	Elem. Anal. C %	H %
F_4 1st trap oil	225	I_1–1	100 15 100	2 400 5 350	$1.4350^{25°}$	$0.7747^{20°}$	169	85.32	14.75
F_4 2nd trap oil	,,	,,	,, ,, ,,	,,	—	$0.7286^{20°}$	113	85.92	14.83
F_4 Wax	,,	,,	,, ,, ,,	,,	$1.4340^{65°}$ m.p. (58.6°–64.4°)	—	328	84.87	15.19
F_5 1st trap oil	225	I_2–1	100 20 100	2 400 5 350	$1.4211^{20°}$	$0.754^{20°}$	144	84.98	15.04
F_5 2nd trap oil	,,	,,	,, ,, ,,	,,	—	$0.6622^{0°}$	85	85.18	15.44
F_{30}(A–D) 1st trap oil	200	XII_{11}–1	100 5 100	5 400 5 350	$1.4319^{20°}$	$0.754^{25°}$	154	85.41	15.05
F_{30}(A–D) 2nd trap oil	,,	,,	,, ,, ,,	,,	$1.4090^{20°}$	—	102	84.45	15.55
F_{31}(A–G) 1st trap oil	200	XII_9–1	100 10 100	5 400 5 350	$1.4239^{20°}$	$0.746^{25°}$	149	84.87	14.84
F_{31}(A–G) 2nd trap oil	,,	,,	,, ,, ,,	,,	—	$0.707^{25°}$	—	84.74	14.87
F_{32}(A–E) 1st trap oil	200	XII_4–1	100 20 100	5 400 5 375	$1.4317^{20°}$	$0.762^{25°}$	167	85.05	14.50
F_{32}(A–E) 2nd trap oil	,,	,,	,, ,, ,,	,,	—	—	—	—	—
F_{33}(A–D) 1st trap oil	200	XII_5–1	100 30 100	5 400 5 375	$1.4320^{20°}$	$0.765^{25°}$	166	84.53	14.97
F_{33}(A–D) 2nd trap oil	,,	,,	,, ,, ,,	,,	—	—	—	—	—
F_{35}(A–D) 1st trap oil	200	XII_8–1	100 48 100	5 400 5 375	$1.4297^{20°}$	—	—	84.50	15.16
F_{36}(A–D) 1st trap oil	200	XII_3–1	100 15 100	5 400 5 375	$1.4229^{20°}$	$0.745^{25°}$	143	85.56	15.00
F_{36}(A–D) 2nd trap oil	,,	,,	,, ,, ,,	,,	$1.4030^{22°}$	$0.668^{25°}$	90	84.19	15.51
F_{37}(A–D) 1st trap oil	200	XII_7–1	100 5 100 +5% ThO_2	5 400 5 375	—	—	—	—	—
F_{37}(A–D) 2nd trap oil	,,	,,	,,	,,	—	—	—	—	—
F_{38}(A–H) 1st trap oil	200	XII_6–1	100 5 100 +5% Cu	5 400 5 375	$1.4313^{20°}$	—	—	84.71	15.25

Table 6.—(*Concluded*)

Exp. No.	Reaction Temp. (°C)	Catalyst No.	Catalyst Comp. $CO+ThO_2+$ Kieselguhr	Pretreatment hrs. °C	Physico-Chem. Properties: Ref. Ind.	Sp. Gr.	App. M. W.	Elem. Anal. C %	H %
F_{38}(A–H) 2nd trap oil	,,	,,	,,	,,	$1.3980^{20°}$	$0.685^{20°}$	85	84.24	15.62
F_{40}(A–G) 1st trap oil	200	XII_{11}–1	100 15 100 +15% ThO_2	5 400 5 375	$1.4319^{20°}$	$0.766^{20°}$	153	85.69	14.42
F_{40}(A–G) 2nd trap oil	,,	,,	,,	,,	$1.4071^{20°}$	$0.702^{20°}$	90	85.08	15.23

Fifth Column; Indicates heat treatment prior to H_2 reduction and temperatures of H_2 reduction, respectively, in the order as written from the top.

Refractive index was determined by using Pulfrich refractometer, and the apparent molecular weights were determined by means of the freezing-point lowering method. The specific gravity was measured by using an ordinary pycnometer whose size was conveniently made as suitable to its respective amount of specimen.

Summary.

(1) Experimental apparatus for studying the catalytic mechanism for the Fischer-Tropsch synthesis with various different types of catalysts has been described and discussed (Series II).

(2) Influences of the CeO_2 content on the cobalt type catalyst as well as ThO_2 content along with the effect of Cu on the catalytic activity, as estimated by the average gas contraction, have been investigated.

(3) Typical gas analysis data for the effluent gas for each of these runs have been tabulated.

(4) Some of the physico-chemical properties of the reaction products have been determined and tabulated.

In conclusion, the authors take this occasion to express their sincere thanks to Dr. T. Marusawa, former Director of the Institute, and Dr. M. Sato, Director of the Institute, for their interests and encouragement during these series of investigations and also for the permission of the publication and we thank Messrs. Kuwabara, Igarashi, Fujiwara and Konoha who have assisted us willingly in the experimental part of this investigation.

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