Physico-Chemical Investigations on Catalytic Mechanism. IX. On the Fischer-Tropsch Synthesis of Hydrocarbons with Special Reference to Factors essential to the Particular Catalysts. (Experimental Series II) (5).

By Senzo **HAMAI**, Shiro **HAYASHI** and Kiyoshi **SHIMAMURA**.

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Introduction. We have been publishing a series of experimental results essential in correlating and systematizing factors which may possibly throw a light upon developing a theory of the reaction mechanism for the Fischer-Tropsch synthesis of hydrocarbons. The present paper, being one of these series, mainly deals with the results obtained with the catalysts(*) composed of Co, U_3O_8, Cu, Mn and Kieselguhr and especially those effects of the reaction temperatures, rate of gas flow, pretreatments and promoters, such as U_3O_8, Cu and Mn, upon the catalytic activity.

Experimental Materials. Hydrogen and carbon monoxide involved in the reaction were prepared similarly as already described in our earlier papers(1).

The materials used in the preparations of the catalysts were nitrates of cobalt, uranium, copper and manganese of which quality is as follows:

$Co(NO_3)_2 \cdot 6H_2O$	Extra pure (Kojima)
$UO_2(NO_3)_2 \cdot 6H_2O$	" " "
$Cu(NO_3)_2 \cdot 3H_2O$	Guaranteed reagent (Kojima)
$Mn(NO_3)_2 \cdot 6H_2O$	" " (Katayama)
K_2CO_3	Extra pure (Kojima)
Kieselguhr (Purified)(2)	

The calculated amount of these materials were taken for the specified catalyst composition, and precipitated by 2 N K_2CO_3 solution as carbonates, washed thoroughly with hot distilled water(3) at least ten times until it became entirely free from the adsorbed nitrate ions and other possible impurities, then dried at 100–110°C. and finally made into small sized tablets by tablet machine.

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(1) Our Reports, IV, this Bulletin, **17** (1942), 166,
V, this Bulletin, **17** (1942), 252,
VI, this Bulletin, **17** (1942), 339,
VII, *J. Chem. Soc. Japan*, **63** (1942), No. 11.
VIII, this Bulletin, **17** (1942), 451.

(2) IV, this Bulletin, **17** (1942), 166.

(3) S. Hamai, *Science* (Iwanami), **11** (1941), 518.

(*) For this type of catalyst, see: S. Tsutsumi, *Report of the Fuel Institute, Japan*, No. 31, 1935.

Experimental Procedure. The catalyst thus made was pretreated as specified in the tables, and when the catalyst zone was ready for a run, a H_2–CO mixture (2:1) was passed over it at the specified temperatures with a definite rate of gas flow (4–8l./hr.); and the gas contraction percentage was measured from time to time.

The reaction products were collected in two separate portions, similarly as those described in our previous papers⑴. The reaction products obtained were later subjected to the determinations of physicochemical constants such as refractive index, specific gravity, apparent molecular weight and elementary analysis. The effluent gas was subjected to gas analysis using a modified form of Orsat gas analysis apparatus, for their constituents.

Experimental Results and Discussions. Some of the experimental results are tabulated and graphically represented. Most of the tables are self-explanatory, but, for the sake of thoroughness, we shall explain them briefly. In Tables 1–8, the gas analysis data for the effluent gas from the typical runs for the specified condition of the catalyst V_1–1, Co+12% U_3O_8+2.5% Cu+100% Kieselguhr are shown. From these data, we are convinced that at the initial stage, the methane formation predominates, as often we have called attention in our previous papers⑴⑷; however, the duration in which CH_4 forms may differ depending on such experimental conditions as the reaction temperatures, rate of gas flow as well as pre-treatments. As regards the formations of CO_2, we may

Table 1.

F_{20}–A, V_1–1_1, Co+12% U_3O_8+2.5% Cu+100% Kieselguhr,
Heat treatment, 400°C., 4 hrs., (Prior to H_2 Reduction).
Reduction, 270°C., 5 hrs. by H_2.
Reaction Temp., 225°C., (4.5 hrs., Exp.).
Contraction, 66%.
Space Velocity, 346.
Rate of Flow, 4 l./hr.; CO:H_2=1:2.

Gas Analysis Data.

	1	2	3
CO_2	0.0	2.0	9.4
C_2H_2	0.0	0.0	0.0
C_2H_4	0.2	0.0	0.4
C_nH_{2n}	0.0	0.0	0.2
O_2	0.4	0.5	0.4
CO	0.0	0.0	13.1
H_2	97.4	85.3	59.2
CH_4	0.0	9.7	15.2
C_2H_6	0.0	0.0	0.0
N_2	2.0	2.5	2.1

⑷ VII, *J. Chem. Soc. Japan*, **63** (1942), No. 11.
VIII, this Bulletin, **17** (1942), 451.

Table 2.

F_{20}–B, (Continued from F_{20}–A)
Reaction Temp., 225°C., 13 hrs. Exp.
Contraction, 70%.

Gas Analysis Data.

	1	2	3	4	5	6	7
CO_2	5.7	7.7	13.8	13.8	12.0	9.6	9.6
C_2H_2	0.0	0.0	0.0	0.0	0.0	0.0	0.2
C_2H_4	0.6	0.0	1.3	0.7	0.8	1.2	1.2
C_nH_{2n}	0.3	0.0	0.3	0.4	0.2	0.0	0.0
O_2	0.4	0.5	0.7	0.5	0.4	0.3	0.4
CO	18.5	21.2	18.3	14.6	15.1	18.2	18.6
H_2	59.7	52.8	45.7	51.4	54.5	57.1	56.0
CH_4	14.1	14.4	17.1	14.3	15.2	10.3	10.2
C_2H_6	0.0	0.0	0.0	2.0	1.8	1.9	1.9
N_2	1.6	2.3	2.8	2.3	1.8	1.4	1.9

Table 3.

F_{20}–C, (Continued from F_{20}–B)
Reacton Temp., 200°C., 220°C.
Contraction, 12%, 68%, (12 hrs. Exp.).

Gas Analysis Data.

	1	2	3	4	5	6
CO_2	2.0	0.7	0.7	3.5	6.5	5.7
C_2H_2	0.0	0.0	0.0	0.0	0.0	0.0
C_2H_4	0.6	0.3	0.4	0.4	1.4	1.0
C_nH_{2n}	0.2	0.0	0.0	0.2	0.0	0.0
O_2	0.6	0.4	0.3	0.3	0.5	0.4
CO	30.2	32.0	32.0	27.0	23.1	24.6
H_2	63.6	64.8	65.2	62.4	58.3	59.5
CH_4	0.0	0.0	0.0	4.6	5.1	5.7
C_2H_6	0.0	0.0	0.0	0.0	2.0	1.3
N_2	2.8	1.8	1.4	1.3	2.1	1.8
		(200°C.)			(220°C.)	

Table 4.

F_{20}–D, (Continued from F_{20}–C),
Reaction Temp., 210°C
Contraction, 35% (6 hrs. Exp.).

Gas Analysis Data.

	1	2	3	4
CO_2	5.4	2.6	1.0	0.9
C_2H_2	0.0	0.0	0.0	0.0
C_2H_4	1.3	0.8	0.8	0.7
C_nH_{2n}	0.0	0.0	0.2	0.0
O_2	0.3	0.3	0.4	0.3
CO	25.0	28.8	29.9	30.3
H_2	57.3	59.5	65.6	66.3
CH_4	7.9	5.8	0.0	0.0
C_2H_6	1.3	0.0	0.0	0.0
N_2	1.5	2.2	1.9	1.5

Table 5.

F_{20}–E, (Continued from F_{20}–D)
Re-reduction, 350°C., by H_2, 2 hrs.
Reaction Temp., 225°C. (4 l./hr.).
Contraction, 60%, (8 hrs. Exp.).

Gas Analysis Data.

	1	2	3	4	5
CO_2	0.0	0.0	5.0	5.6	4.2
C_2H_2	0.0	0.0	0.0	0.0	0.0
C_2H_4	0.4	0.2	0.4	0.9	0.8
C_nH_{2n}	0.0	0.0	0.0	0.0	0.3
O_2	0.3	0.3	0.4	0.3	0.4
CO	0.0	0.0	1.6	13.8	22.3
H_2	97.4	81.4	76.9	64.0	58.0
CH_4	0.0	5.6	4.3	11.6	12.1
C_2H_6	0.0	0.0	5.7	2.1	2.4
N_2	1.9	1.5	1.7	1.7	1.9

Table 6.

F_{20}–F, (Continued from F_{20}–E)
Reaction Temp. 225°C.,
Rate of Flow, 8 l./hr. 6 l./hr.
Contraction, 25% 25% (12 hrs. Exp.).

Gas Analysis Data.

	1	2	3	4	5	6	7
CO_2	6.0	9.0	1.0	0.3	0.3	0.4	0.5
C_2H_2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C_2H_4	0.9	0.6	0.8	0.6	0.7	0.7	0.9
C_nH_{2n}	0.0	0.2	0.0	0.0	0.0	0.0	0.0
O_2	0.4	0.5	0.4	0.2	0.3	0.4	0.2
CO	19.7	10.7	30.7	31.6	31.1	31.2	31.4
H_2	59.2	58.5	65.1	65.9	66.1	65.6	65.7
CH_4	8.8	17.6	0.0	0.0	0.0	0.0	0.0
C_2H_6	3.2	0.0	0.0	0.0	0.0	0.0	0.0
N_2	1.8	2.5	2.0	1.4	1.5	1.7	1.3
	(8 l./hr.)				(6 l./hr.)		

Table 7.

F_{20}–G, (Continued from F_{20}–F)
Reaction Temp., 230°C.
Rate of Flow, 8 l./hr., 6 l./hr.
Constraction, 40%, 42% (13 hrs. Exp.).

Gas Analysis Data.

	1	2	3	4	5	6	7	8
CO_2	2.0	2.4	2.0	1.2	1.4	1.3	1.8	1.0
C_2H_2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C_2H_4	0.8	1.1	1.4	1.0	1.2	1.4	1.9	1.2
C_nH_{2n}	0.0	0.2	0.0	0.3	0.3	0.0	0.2	0.5
O_2	0.3	0.4	0.4	0.5	0.4	0.3	0.3	0.5
CO	30.0	27.4	28.5	29.4	29.8	30.7	29.5	30.0
H_2	65.5	59.5	60.6	60.0	64.8	61.3	61.1	64.0
CH_4	0.0	4.7	4.0	4.4	0.0	2.6	2.1	0.0
C_2H_6	0.0	1.6	1.3	1.4	0.0	1.0	1.8	0.0
N_2	1.4	1.7	1.8	1.4	2.1	1.4	1.3	2.8
	(8 l./hr.)				(6 l./hr.)			

Table 8.

F_{20}–H, (Continued from F_{20}–G)
Reaction Temp., 230°C. (4 l./hr.)
Contraction, 50% (7 hrs. Exp.).

Gas Analysis Data.

	1	2	3	4
CO_2	2.2	3.3	3.8	3.0
C_2H_2	0.0	0.2	0.0	0.0
C_2H_4	1.4	1.3	1.2	1.3
C_nH_{2n}	0.4	0.3	0.0	0.2
O_2	0.5	0.4	0.4	0.3
CO	26.5	27.4	25.9	26.4
H_2	60.2	59.6	60.7	60.4
CH_4	5.0	4.3	5.0	5.4
C_2H_6	0.5	1.3	1.2	1.4
N_2	2.3	1.9	1.8	1.6

possibly state that they are somewhat parallel with the methane formations, as clearly shown in these tables; of course, a strict proportionality may not be expected, since the reaction system is quite complex and furthermore they are outcome of the combinations of the reactions, such as (1) $Co+3H_2=CH_4+H_2O$ and (2) $CO+H_2O=H_2+CO_2$ and of the combination of these two (3) $2CO+2H_2=CH_4+CO_2$, as well as (4) $CO_2+4H_2=CH_4+2H_2O$, and also of these reactions; the extents of the equilibria as well as the reaction speed are connected with various factors and expected to be inter-related. Judging these reactions and our results as regards the formations of CH_4 annd CO_2 as well as H_2O, the explanations seem to be rather reasonable, especially with regard to the initial stage of the reaction prior to normalization of the reaction system.

In Tables 9–11, the results are given for the effects of promoters, such as U_3O_8, Cu in various different percentages, and of Mn. As seen in Table 9, for these particular catalysts, as far as the copper content is concerned, 2.5% Cu seemed to be optimal among those tested in this range of percentages. Here we also are convinced that the average gas contraction percentage may not necessarily be parallel with the order of

Table 9. Effects of Promoters.

Type of Catalyst, $Co+12\%U_3O_8+x\%Cu+100\%$ Kieselguhr
Rate of gas Flow; 4 l./hr.; $CO:H_2=1:2$

Cu (%)	React. Temp. (°C.)	Exp. No.	Ave. Gas Cont. (%)	Oil Yields c.c./m^3	Remarks			
					Heat Treat.		H_2 Reduct.	
					(°C.)	(hrs.)	(°C.)	(hrs.)
					(400)	(4)	(270)	(5) (F_{20}–A)
2.5	200	F_{20}–C	12	28.5	—	—	—	—
	220	„	68	147	—	—	—	—
	210	F_{20}–D	36	26.9	—	—	—	—
	230	F_{20}–H	50	131.3	—	—	350	2
	225	F_{19}–E	40	173	400	5	350	5
5	200	F_{21}–B	52	18	400	2	250	5
	190	F_{21}–D	30	20	—	—	210	2
	225	F_{21}–E	70	46	—	—	350	2
	200	F_{21}–H	30	80	—	—	230	2
10	200	F_{22}–A	57	3.9	400	2	230	5
	„	F_{22}–B	32	56	—	—	300	2
					(400)	(5)	(270)	(5) (F_{23}–A)
0	200	F_{23}–E	20	46	—	—	370	2
	225	„	30	—	—	—	—	—
	„	F_{23}–G	24	63.3	—	—	300	2

Table 10. Effects of Promoters.

Type of Catalyst, $Co+x\%U_3O_8+2.5\%Cu+100\%$ Kieselguhr
Rate of gas Flow, 4 l./hr.; $CO:H_2=1:2$

U_3O_8 (%)	React. Temp. (°C.)	Exp. No.	Ave. Gas Cont. (%)	Oil Yields c.c./m^3	Remarks			
					Heat Treat.		H_2 Reduct.	
					(°C.)	(hrs.)	(°C.)	(hrs.)
					(400)	(4)	(270)	(5) (F_{20}–A)
12	225	F_{20}–B	70	123	—	—	—	—
					(400)	(5)	(270)	(5) (F_{26}–A)
15	„	F_{26}–C	66	93	—	—	—	—

Table 11. Effects of Promoters.

Type of Catalyst, $Co+12\% U_3O_8+5\% Cu+x\% Mn+100\%$ Kieselguhr
Rate of Gas Flow, 4 l./hr.; $CO:H_2=1:2$

Mn (%)	React. Temp. (°C.)	Exp. No.	Ave. Gas Cont. (%)	Oil Yields c.c./m³	Remarks			
					Heat Treat.		H_2 Reduct.	
					(°C.)	(hrs.)	(°C.)	(hrs.)
4	200	F_{29}–A	3	43	400	5	300	5
	270	F_{29}–B	66*	24	—	—	—	—
	250	F_{29}–C	40	45	—	—	—	—
					(400)	(2)	(250)	(5) (F_{21}–A)
0	190	F_{21}–D	30	20	—	—	210	2
	225	F_{21}–F	66*	7.1	—	—	300	2
	200	F_{21}–H	30	80	—	—	230	2

* Large amount of CH_4 formation.

oil yields, as often we have called attention in our earlier papers⁽⁵⁾. In Table 10, the results with 12 and 15% U_3O_8 are compared. In Table 11, the effects of Mn are compared. Although no definite conclusion may be drawn from these meager data, we may conservatively state that the effects of Mn is not distinct; however, as far as these data allow, a catalyst without Mn seems to be more desirable. In Table 12 the effects of a carrier, Kieselguhr, for this particular catalyst are compared.

Table 12. Effects of Carrier, Kieselguhr.

Type of Catalyst, $Co+12\% U_3O_8+2.5\% Cu+x\%$ Kieselguhr
Rate of Gas Flow, 4 l./hr.; $CO:H_2=1:2$

Kiesel. (%)	React. Temp. (°C.)	Exp. No.	Ave. Gas Cont. (%)	Oil Yields c.c./m³	Remarks			
					Heat Treat.		H_2 Reduct.	
					(°C.)	(hrs.)	(°C.)	(hrs.)
100	225	F_{20}–A	66**	38.8	400	4	270	5
”	”	F_{20}–B	70	122.6	—	—	—	—
”	200	F_{20}–C	12	28.5	—	—	—	—
”	220	”	68	146.9	—	—	—	—
0	225	F_{24}–A	66*	3.4	400	5	300	5
”	”	F_{24}–B	66*	9.3	—	—	”	2
”	”	F_{24}–C	62*	14.5	—	—	350	”
”	”	F_{24}–D	64*	2.6	400	2	”	5
”	”	F_{25}–A	66*	0	400	5	270	”
”	”	F_{25}–B	64*	0	—	—	350	2

* Large amount of CH_4 formation.
** CH_4 formation at the initial stage.

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(5) S. Hamai, S. Hayashi, K. Shimamura and H. Igarashi, this Bulletin, **17** (1942), 166; S. Hamai, this Bulletin, **17** (1942), 339.

Here we can see definitely the superiority of the catalyst with the carrier, and with the catalyst contaianing no Kieselguhr contributes almost nothing to the oil formation reaction but the methane formation. As far as the contraction percentage is concerned, both cases are of comparable order. These results clearly demonstrate the importance of segregation of catalytic activities due to each particular reaction, as that of methane formation and that of oil formation, when we discuss the catalytic activities as judged from the gas contraction alone. From these data, we can clearly see that the contraction percentages, namely, 66%, indicated for the catalyst with no Kieselguhr, is practically entirely due to the reaction (I) $CO+3H_2=CH_4+H_2O$, forming a large amount of methane and water which in turn reacts with CO and gives $CO+H_2O=H_2+CO_2$. Thus we see a large amount of CO_2 formation, somewhat in parallel with the methane formation. (The maximum contraction available from the reaction (I) alone is $66^2/_3\%$). Furthermore, in these cases practically no oil formation was observed, at least a very small amount—if any.

In Tablels 13–17, those effects of the reaction temperature on the activity for various different catalysts as judged from the gas contraction percentages, oil yields, as well as principal gaseous products are compared at several different temperatures.

In main, when the temperature(4) is higher, gaseous products, such as CH_4 and CO_2, predominate for every catalyst tested, with a considerable magnitude of gas contraction and a very small amount of oil formation. This is very reasonable, considering that these reactions, mentioned already, predominate at these particular conditions, especially when the reaction system is not well normalized. Here we see also the optimal

Table 13. Effects of the Reaction Temperature on the Activity.

Type of Catalyst, $Co+12\%U_3O_8+2.5\%Cu+100\%$ Kieselguhr
Rate of Gas Flow, 4 l./hr.. $CO:H_2=1:2$

Exp. No.	React. Temp. (°C.)	Ave. Gas Cont. (%)	CO_2	C_2H_4	CH_4	C_2H_6	Oil Yields c.c./m³	Remarks			
								Heat Treat.		H_2 Reduct.	
								(°C.)	(hrs.)	(°C.)	(hrs.)
								400	5	350	5*
F_{19}–E	225	40	0.8	1.6	0.0	0.0	173	—	—	—	—
F_{19}–L	250	70	9.2	0.5	12.0	0.0	103	400	5	270	2
								400	4	270	5**
F_{19}–R	230	44	0.7	0.5	0.0	0.0	—	—	—	—	—
F_{19}–S	235	44	1.6	0.6	0.0	0.0	—	—	—	—	—
								400	4	270	5†
F_{20}–B	225	70	9.6	1.2	10.2	1.9	123	—	—	—	—
F_{20}–C	220	68	0.7	0.3	0.0	0.0	147	—	—	—	—
F_{20}–D	210	36	0.9	0.7	0.0	0.0	27	—	—	—	—
										350	2‡
F_{20}–H	230	50	3.8	1.2	5.0	1.2	131.3	—	—	—	—

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* (F_{19}–A); ** (F_{19}–Q); † (F_{20}–A); ‡ (F_{20}–E).

Table 14. Effects of the Reaction Temperature on the Activity.

Type of Catalyst, Co+12% U_3O_8+5% Cu+100% Kieselguhr
Rate of Gas Flow, 4 l./hr., CO:H_2=1:2

Exp. No.	React. Temp. (°C.)	Ave. Gas Cont. (%)	CO_2	C_2H_4	CH_4	C_2H_6	Oil Yields c.c./m³	Remarks			
								Heat Treat.		H_2 Reduct.	
								(°C.)	(hrs.)	(°C.)	(hrs.)
F_{21}–A	200	60*	15.3	0.2	38.9	2.7	0	400	2	250	5
F_{21}–C	190	22	0.2	0.5	0.0	0.0	54.4	—	—	230	2
	200	44	0.6	0.5	0.0	0.0	—	—	—	—	—
F_{21}–D	190	30	0.3	0.6	0.0	0.0	—	—	—	210	2
	200	32	0.5	0.5	0.0	0.0	20	—	—	—	—
	225	80	7.0	0.7	11.2	3.9	—	—	—	—	—
F_{21}–E	190	23	0.2	0.4	0.0	0.0	46.1	—	—	350	2
	200	30	0.5	0.2	0.0	0.0	—	—	—	—	—
	225	70	0.2	0.4	0.0	0.0	—	—	—	—	—
F_{21}–H	200	30	0.5	0.7	0.0	0.0	80.0	—	—	230	2
With 10% Cu											
								400	2	230	5**
F_{22}–B	200	32	0.2	0.5	0.0	0.0	56	—	—	300	2

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* (F_{22}–A).

Table 15. Effects of the Reaction Temperature on the Activity.

Type of Catalyst, Co+12% U_3O_8+100% Kieselguhr
Rate of Gas Flow, 4 l./hr., CO:H_2=1:2

Exp. No.	React. Temp. (°C.)	Ave. Gas Cont. (%)	CO_2	C_2H_4	CH_4	C_2H_6	Oil Yields c.c./m³	Remarks			
								Heat Treat.		H_2 Reduct.	
								(°C.)	(hrs.)	(°C.)	(hrs.)
F_{23}–A	200	20	0.2	0.2	0.0	0.0	12	400	5	270	5
F_{23}–E	200	20	0.0	0.0	0.0	0.0	46	—	—	370	2
	225	30	0.2	0.2	0.0	0.0	—	—	—	—	—
F_{23}–F	225	32	0.3	0.2	0.0	0.0	22	—	—	300	2
F_{23}–G	225	24	0.2	0.2	0.0	0.0	63.3	—	—	—	—

Table 16. Effects of the Reaction Temperature on the Activity.

Type of Catalyst, Co+12% U_3O_8+2.5% Cu
Rate of Gas Flow, 4 l./hr.; CO:H_2=1:2

Exp. No.	React. Temp. (°C.)	Ave. Gas Cont. (%)	CO_2	C_2H_4	CH_4	C_2H_6	Oil Yields c.c./m³	Remarks			
								Heat Treat.		H_2 Reduct.	
								(°C.)	(hrs.)	(°C.)	(hrs.)
F_{24}–A	225	66*	17.7	0.2	62.2	0.0	3.4	400	5	300	5
F_{24}–B	"	66*	13.4	0.0	50.2	0.0	9.3	—	—	300	2
F_{24}–C	"	62*	12.1	0.0	47.1	0.0	14.5	—	—	350	2
F_{24}–D	"	64*	14.0	0.4	53.5	0.0	—	400	2	350	5
	200	15	1.1	0.2	0.0	0.0	2.6	—	—	—	—
F_{24}–E	200	2	0.2	0.3	0.0	0.0	2.2	—	—	—	—
F_{25}–A	225	66*	14.5	0.4	59.1	0.0	—	400	5	270	5
F_{25}–B	"	64*	14.1	0.4	54.4	0.0	—	—	—	350	2

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* Large amount of CH_4 formation.
** (F_{22}–A).

Table 17. Effects of the Reaction Temperature on the Activity.

Type of Catalyst, $Co+12\%U_3O_8+5\%Cu+4\%Mn+100\%$Kieselguhr
Rate of Gas Flow, 4 l./hr.; $CO:H_2=1:2$

Exp. No.	React. Temp. (°C.)	Ave. Gas Cont. (%)	CO_2	C_2H_4	CH_4	C_2H_6	Oil Yields c.c./m^3	Remarks Heat Treat. (°C.)	(hrs.)	H_2 Reduct. (°C.)	(hrs.)
F_{29}–A	200	3	0.0	0.2	0.0	0.0	43	400	5	270	5
F_{29}–B	270	66*	18.0	0.4	23.8	8.0	24	—	—	—	—
F_{29}–C	250	40	3.9	1.1	0.0	0.0	45	—	—	—	—
$Co+15\%U_3O_8+2.5\%Cu+100\%$ Kieselguhr											
F_{26}–A	225	70*	6.9	0.3	29.2	1.0	50	400	5	270	5
F_{26}–B	”	74	5.0	2.1	10.2	9.2	73	—	—	—	—
F_{26}–C	”	66	3.9	1.8	7.3	6.2	93	—	—	—	—
F_{26}–D	”	64*	5.1	1.9	15.4	3.3	52	—	—	—	—
F_{26}–E	”	32	0.2	0.3	0.0	0.0	48	400	5	350	5

* Large amount of CH_4 formation.

reaction temperature for the particular catalyst; among these data we may possibly state that 225°C. is the optimal for the majority of these catalysts except for those without Kieselguhr. This catalyst, as shown in Table 16, may not be considered as desirable as far as the oil formation is concerned although the activity for the formation of gaseous products, such as CH_4 and CO_2, is very high.

In Tables 18–23, those effects of various pretreatments upon the catalytic activity as judged by the average gas contraction, oil yields, and gaseous products, at several different reaction temperatures are shown. Regarding the initial reduction temperature, the presence of Cu seems to lower the reduction temperature. This is in concordance with the fact found in the literature(6). For the catalyst, $CO+12\%U_3O_8+2.5\%Cu+100\%$ Kieselguhr, by the H_2 pretreatment at relatively low temperature such as 270°C., as compared with the initial pretreatment temperature 350°C., the once decayed activity may be restored as in the series of F_{19}; while in the series of F_{20}, the decayed activity equally is recovered with the reversed order of pretreatments, namely, initially at 270°C., 5 hrs. then at 350°C. 2 hrs., but we may find a difference in the formation of gaseous products, i.e., CH_4 and CO_2 formations are more persistent in the series of F_{20}.

As seen in Tables 19–20, we may say that there is some optimal pretreatment temperature to get a fairly good activity although in every case the methane formation may be found immediately after pretreatment.

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(6) (a) F. Fischer and H. Koch, *Brenn-Chem.*, **13** (1932), 61.
(b) S. Tsutsumi, *Report of Fuel Research Institute, Japan*, No. 31 (1935).
(c) S. Tsuneoka, "Synthetic Liquid Fuel" (in Japanese) pp. 66, 67, 68, 86, 87 (1938).

Table 18. Effects of Pre-treatments.

Type of Catalyst, $Co+12\%U_3O_8+2.5\%Cu+100\%$ Kieselguhr
Rate of Gas Flow, 4 l./hr.; $CO:H_2=1:2$

Exp. No.	React. Temp. (°C.)	Pre-treatments				Ave. Gas Cont. (%)	Oil Yields $\mathrm{c.c./m^3}$	CO_2 (%)	C_2H_4 (%)	CH_4 (%)	C_2H_6 (%)
		Heat Treat.		H_2 Red.							
		(°C.)	(hrs.)	(°C.)	(hrs.)						
		400	5	350	5	(F_{19}–A)					
F_{19}–E	225	—	—	—	—	40	173	0.8	1.6	0.0	0.0
F_{19}–L	250	400	5	270	2	70	103	9.2	0.5	12.0	0.0
F_{19}–N	225	—	—	—	—	25	50	0.6	0.9	0.0	0.0
F_{19}–Q	225	400	2	270	5	22	—	0.5	0.6	0.0	0.0
F_{19}–R	230	—	—	—	—	44	—	0.7	0.5	0.0	0.0
F_{19}–S	235	—	—	—	—	44	—	1.6	0.6	0.0	0.0
		400	4	270	5	(F_{20}–A)					
F_{20}–B	225	—	—	—	—	70	123	9.6	1.2	10.2	1.9
F_{20}–C	220	—	—	—	—	68	147	6.5	1.4	5.1	2 0
F_{20}–E	225	—	—	350	2	64	70	4.2	0.8	12.1	2.4
F_{20}–H	230	—	—	—	—	50	131.3	3.8	1.2	5.0	1.2

Table 19. Effects of Pre-treatments.

Type of Catalyst, $Co+12\%U_3O_8+5\%Cu+100\%$ Kieselguhr
Rate of Gas Flow, 4 l./hr.; $CO:H_2=1:2$

Exp. No.	React. Temp. (°C.)	Pre-treatments				Ave. Gas Cont. (%)	Oil Yields $\mathrm{c.c./m^3}$	CO_2 (%)	C_2H_4 (%)	CH_4 (%)	C_2H_6 (%)
		Heat Treat.		H_2 Red.							
		(°C.)	(hrs.)	(°C.)	(hrs.)						
F_{21}–A	200	400	2	250	5	60	0	15.3	0.2	38.9	2.7
F_{21}–C	"	—	—	230	2	44	54	0.6	0.5	0.0	0.0
F_{21}–D	"	—	—	210	2	32	20	0.5	0.5	0.0	0.0
F_{21}–E	"	—	—	350	2	30	46	0.5	0.2	0.0	0.0
F_{21}–F	"	—	—	300	2	36	7	0.7	0.3	0.0	0.0
F_{21}–H	"	—	—	230	2	30	80	0.5	0.7	0.0	0.0

Table 20. Effects of Pre-treatments.

Type of Catalyst, $Co+12\%U_3O_8+10\%Cu+100\%$ Kieselguhr
Rate of Gas Flow, 4 l./hr.; $CO:H_2=1:2$

Exp. No.	React. Temp. (°C.)	Pre-treatments				Ave. Gas Cont. (%)	Oil Yields $\mathrm{c.c./m^3}$	CO_2 (%)	C_2H_4 (%)	CH_4 (%)	C_2H_6 (%)
		Heat Treat.		H_2 Red.							
		(°C.)	(hrs.)	(°C.)	(hrs.)						
F_{22}–A	200	400	2	230	5	57	4	14.0	0.3	1.9	0.0
F_{22}–B	"	—	—	300	2	32	56	0.2	0.5	0.0	0.0
F_{22}–C	"	—	—	350	2	16	2.4	0.3	0.2	0.0	0.0
F_{22}–D	"	—	—	270	2	20	35	0.0	0.2	0.0	0.0

Table 21. Effects of Pre-treatments.

Type of Catalyst, $Co+12\%U_3O_8+100\%$ Kieselguhr
Rate of Gas Flow, 4 l./hr., $CO:H_2=1:2$

Exp. No.	React. Temp. (°C.)	Pre-treatments				Ave. Gas Cont. (%)	Oil Yields c.c./m³	CO_2 (%)	C_2H_4 (%)	CH_4 (%)	C_2H_6 (%)
		Heat Treat. (°C.)	Heat Treat. (hrs.)	H_2 Red. (°C.)	H_2 Red. (hrs.)						
F_{23}–A	200	400	5	270	5	20	12	0.2	0.2	0.0	0.0
F_{23}–B	”	—	—	300	2	15	19	0.2	0.2	0.0	0.0
F_{23}–C	”	—	—	350	2	10	18	0.0	0.3	0.0	0.0
F_{23}–D	”	—	—	400	2	10	5.5	0.0	0.0	0.0	0.0
F_{23}–E	”	—	—	370	2	20	46	0.0	0.0	0.0	0.0
F_{23}–F	225	—	—	300	2	32	22	0.3	0.2	0.0	0.0
F_{23}–G	”	—	—	—	—	24	63.3	0.2	0.2	0.0	0.0

Table 22. Effects of Pre-treatments.

Type of Catalyst, $Co+12\%U_3O_8+2.5\%Cu$,
Rate of Gas Flow, 4 l./hr.; $CO:H_2=1:2$

Exp. No.	React. Temp. (°C.)	Pre-treatments				Ave. Gas Cont. (%)	Oil Yields c.c./m³	CO_2 (%)	C_2H_4 (%)	CH_4 (%)	C_2H_6 (%)
		Heat Treat. (°C.)	Heat Treat. (hrs.)	H_2 Red. (°C.)	H_2 Red. (hrs.)						
F_{24}–A	225	400	5	300	5	66*	3.4	17.7	0.2	62.2	0.0
F_{24}–B	”	—	—	300	2	66*	9.3	13.4	0.0	50.2	0.0
F_{24}–C	”	—	—	350	2	62*	14.5	12.1	0.0	47.1	0.0
F_{25}–A	225	400	5	270	5	66*	0	14.5	0.4	59.1	0.0
F_{25}–B	”	—	—	350	2	64*	0	14.1	0.4	54.4	0.0

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* An extraordinarily large amount of CH_4 formation was observed. The maximum contraction percentage due to $CO+3H_2=CH_4+H_2O$ alone is 66 2/3%; considering these we may possibly say that our results indicate that the reaction is entirely due to the above reaction. Therefore, this catalyst is to be extraordinarily good for CH_4 formation, but not for oil formation under these conditions.

Table 23. Effects of Pre-treatments.

Type of Catalyst, $Co+15\%U_3O_8+2.5\%Cu+100\%$ Kieselguhr
Rate of Gas Flow, 4 l./hr.; $CO:H_2=1:2$

Exp. No.	React. Temp. (%)	Pre-treatments				Ave. Gas Cont. (%)	Oil Yields c.c./m³	CO_2 (%)	C_2H_4 (%)	CH_4 (%)	C_2H_6 (%)
		Heat Treat. (°C.)	Heat Treat. (hrs.)	H_2 Red. (°C.)	H_2 Red. (hrs.)						
F_{26}–A	225	400	5	270	5	70	50	6.9	0.3	29.2	1.0
F_{26}–B	”	—	—	—	—	74	73	5.0	2.1	10.2	9.2
F_{26}–C	”	—	—	—	—	66	93	3.9	1.8	7.3	6.2
F_{26}–D	”	—	—	—	—	64	52	5.1	1.9	15.4	3.3
F_{26}–E	”	400	5	350	5	32	48	0.2	0.3	0.0	0.0
F_{26}–F	”	—	—	—	—	13	0	0.3	0.2	0.0	0.0

In Table 21, we see that for the catalyst without Cu, the reduction temperature at the initial stage should be fairly high in order to get sufficient activity and the later pretreatment temperature has to be higher for getting a reasonable amount of oil formation.

As observed in Table 22, for the catalyst without Kieselguhr, regardless of differences of pretreatment temperatures, there we found no difference as to the activity in the oil formation, but in every case we found practically the same contraction percentage, with predominating tendency for CH_4 and CO_2 formations. These facts, with the fore-mentioned relations between the oil formation and the pretreatments, imply that there is some delicate connection between the pretreatments and the activity for the oil formation which may be sensitively affected by the porosity of materials as well as the surface structure as varied by these heat treatments. However, a more definite conclusion, though very desirable, cannot be obtained at the present stage.

The lowering of the initial reduction temperature when Cu is present in the catalyst again is demonstrated even for the catalyst which contains 15% U_3O_8, and a fairly low temperature for pretreatment may be adopted for a sufficient activity. These are shown in Table 23.

In Table 24, some of the physico-chemical constants for the products in the series of F_{19}–F_{29} are compiled. In this table, the first trap oil indicates the heavier fraction and the second the lighter one condensed by solid CO_2 -C_2H_5OH mixture.

Table 24. Properties of the Products.

Exp. No.	Ref. Ind. 25°C.	Sp. Gr. 25°C.	App. M. W.	Elem. Analysis	
				C %	H %
F_{19}(A–K) 1st trap	$1.4259^{30°}$	0.759	160	84.79	15.32
F_{19}(A–K) 2nd trap	$1.3850^{30°}$	0.677	88	83.63	15.82
F_{19}(L–P) 1st trap	$1.4212^{30°}$	0.770	179	84.97	15.01
F_{19}(L–P) 2nd trap	$1.3868^{30°}$	0.702	100	84.24	15.84
F_{20}(A–D) 1st trap	$1.4222^{30°}$	0.756	139	85.19	14.73
F_{20}(A–D) 2nd trap	$1.3802^{30°}$	0.685	84	84.39	15.58
F_{20}(E–H) 1st trap	1.4273	0.758	152	84.40	15.68
F_{20}(E–H) 2nd trap	1.3939	0.687	87	83.79	16.07
F_{21}(A–D) 1st trap	1.4219	0.749	130	84.66	15.28
F_{21}(A–D) 2nd trap	1.4034	—	94	83.69	16.21
F_{21}(E–H) 1st trap	—	—	—	83.82	15.81
F_{21}(E–H) 2nd trap	1.4010	0.701	81	83.02	16.76
F_{22}(A–F) 1st trap	$1.4258^{30°}$	—	—	84.33	15.14
F_{32}(A–F) 2nd trap	$1.4080^{30°}$	—	—	—	—
F_{23}(A–I) 1st trap	$1.4273^{30°}$	0.765	177	84.74	15.06
F_{23}(A–I) 2nd trap	$1.4028^{30°}$	0.711	111	83.92	15.20
F_{26}(A–D) 1st trap	$1.4213^{30°}$	0.748	139	85.04	15.29
F_{26}(A–D) 2nd trap	—	0.687	92	84.37	15.42
F_{26}(A–D) 1st trap	$1.4381^{20°}$	—	177	—	—

In Fig. 1, the results for the contraction percentages in the series of F_{20} as a function of the reaction temperature are plotted, while in Fig. 2, the results for the contraction percentages as a function of the rate of gas flow at 225°C. and 230°C., respectively, are plotted.

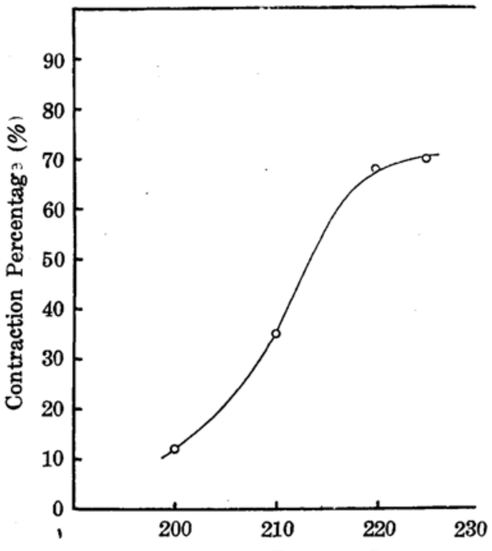

Fig. 1. Gas Contraction Percentage Vs. Reaction Temperature.

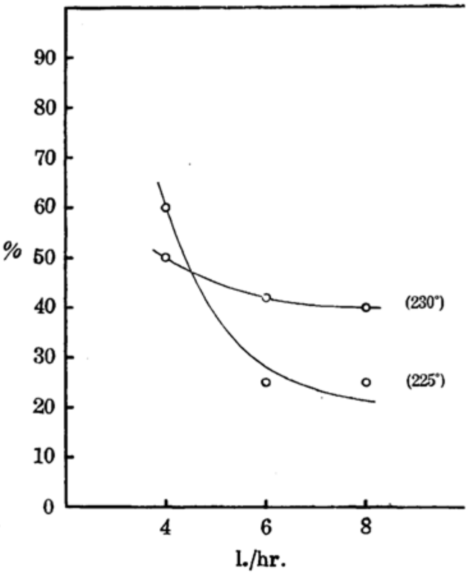

Fig. 2. Contraction % Vs. Rate of Flow.

Thus far, we have presented typical results for the series F_{19}–F_{29}, with respect to the gas analysis data, and the effects of reaction temperature, rate of gas flow, pretreatments, and of promoters. These results are correlated, and some explanations are offered with special reference to the reaction mechanism for the Fischer-Tropsch synthesis of hydrocarbons.

Summary.

(1) The experimental materials used in this investigation are briefly described along with the preparations of the catalysts.

(2) The experimental procedure with reference to our previous paper is presented.

(3) The typical results, as related to the catalytic activity and gaseous products, are tabulated and some correlations are offered.

(4) The effects of such promoters as U_3O_8, Cu, and Mn along with those of a carrier, Kieselguhr, upon the catalytic activity are tabulated and discussed; furthermore, possible correlations with the oil formation are presented.

(5) The results of the effects of the reaction temperature, as well as of the pretreatment upon the activity, with special emphasis on the oil formations and gaseous products are presented and discussed rather thoroughly, and some possible correlations are given.

(6) Finally, the properties of the liquid products for the series of F_{19}–F_{29} for the type of catalysts, $Co+x\%U_3O_8+y\%Cu+z\%Mn+w\%$ Kieselguhr, such as refractive indices, specific gravities, apparent molecular weights and elementary analysis data are compiled in the table.

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The Central Laboratory,
South Manchuria Railway Company, Dairen.