Physico-Chemical Investigations on Catalytic Mechanism. VI. On the Fischer-Tropsch Synthesis of Hydrocarbons. (Experimental Series II)*** (2).

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The present paper being a further report of the series of investigations(1), we shall omit the experimental aspects, but we attempt to describe the results concerning the effects of promoters on the Co type catalyst. Experimental apparatus and detailed experimental procedures have been fully presented in our previous paper(2).

One of the most interesting problems in the catalytic mechanism which have not yet been settled is the role of promoters in the catalytic activity in general. Bearing these in mind, we have carried out the experiments which may possibly throw some light in correlation with the catalytic activity; furthermore, these experimental results clear the way for the systematic explanations of the mechanism. So far many investigators(3) have undertaken the task and contributed much, but on account of the fundamental difficulty to get reproducible results, most experimental results can hardly be considered as reliable as to give a clear-cut, general conclusion. In this sense, we are justified to say that, in such chaotic conditions of numerous results, we are confronted practically with a hopeless situation. For such reasons, the author considers that every bit of experimental results has to be correlated in some such systematic manner as to enable us to get hold of a clear vision of the catalytic mechanism out of such chaotic mass of numerous investigations.

We mainly present the effects of B_2O_3 in our new catalyst and of Cu, the combined effects of ThO_2 and CeO_2, as well as those of pre-treatments of the catalysts.

Experimental Results. The catalyst which we had employed was a series of the catalysts of Co with various promoters such as CeO_2, ThO_2, B_2O_3, and Cu and Kieselguhr as a carrier (support), as shown in our tables; and the method of preparation and experimental procedures were exactly similar to those, already described in our report IV(4).

(***) Most of the results given in this paper was obtained and completed in 1939–1940, but the publication of them has been withheld.

(1) Our reports; I, II, III, IV, and V.
(I) *J. Chem. Soc. Japan*, **62** (1941), 516;
(II) This Bulletin, **16** (1941), 213;
(III) *J. Soc. Chem. Ind. Japan*, **45** (1942), 313;
(IV) This Bulletin, **17** (1942), 166;
(V) This Bulletin, **17** (1942), 252.

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

(3) Series of papers by the schools of Fischer, Kita, and others.

(4) Report IV, this Bulletin, **17** (1942), 166.

Tables 1–4 indicate typical results out of various experiments. As seen in Table 1, the effects of B_2O_3 on the average gas contraction as an approximate measure of the catalytic activity are well detectable. It seemed that the addition of B_2O_3 improved the activity as well as the quality of the products⁽⁵⁾; i.e., in F_{40}(A)–F_{40}(G) series where the catalyst

Table 1.

Effects of B_2O_3

Exp. No.	Catalyst No.	Catalyst Composition (%)					Reaction Temp. (°C.)	Average Contraction (%)
		Co +	CeO_2 +	ThO_2 +	B_2O_3 +	Kieselguhr		
F_{39}(A–I)	XII$_{12}$–1	100	15	15	5	100	200	64
F_{41}(A–E)	XII$_{12}$–1	”	”	”	”	”	”	49
F_{40}(A–G)	XII$_{11}$–1	”	”	”	0	”	”	34
F_{45}(A–H)	XII$_{16}$–1	”	”	”	10	”	”	49
F_{49}(F)	XII$_{16}$–1	”	”	”	10	”	”	42

Table 2.

Effects of B_2O_3 in the Presence of Cu

Exp. No.	Catalyst No.	Catalyst Composition (%)						Reaction Temp. (°C.)	Average Contraction (%)
		Co +	CeO_2+	ThO_2+	B_2O_3 +	Cu+	Kieselguhr		
F_{48}(A–F)	XII$_{19}$–1	100	15	15	10	5	100	200	10
F_{43}(A–I)	XII$_{14}$–1	”	15	15	5	”	”	”	45
F_{47}(A–E)	XII$_{18}$–1	”	18	18	10	”	”	”	25
F_{44}(A–D)	XII$_{15}$–1	”	18	18	5	”	”	”	15

Table 3.

Effects of Cu

Exp. No.	Catalyst No.	Catalyst Composition (%)						Reaction Temp. (°C.)	Average Contraction (%)
		Co +	CeO_2+	ThO_2+	B_2O_3 +	Cu+	Kieselguhr		
F_{48}(A–F)	XII$_{19}$–1	100	15	15	10	5	100	200	10
F_{45}(A–H)	XII$_{16}$–1	”	”	”	”	0	”	”	49
F_{47}(A–E)	XII$_{18}$–1	”	18	18	”	5	”	”	25
F_{46}(A–G)	XII$_{17}$–1	”	”	”	”	0	”	”	65
F_{43}(A–I)	XII$_{14}$–1	”	15	15	5	5	”	”	45
F_{39}(A–I)	XII$_{12}$–I	”	”	”	”	0	”	”	64

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(5) Concerning this point, we shall present the results in our subsequent paper to be published elsewhere. (There is some good evidence that the products seem to contain branched chain hydrocarbons.)

Table 4.

Combined Effects of the ThO_2 and CeO_2 Contents

Exp. No.	Catalyst No.	Catalyst Composition (%)						Reaction Temp. (°C.)	Average Contraction (%)
		Co +	CeO_2+	ThO_2+	B_2O_3 +	Cu+	Kieselguhr		
F_{44}(A–D)	XII_{15}–1	100	18	18	5	5	100	200	15
F_{43}(A–I)	XII_{14}–1	”	15	15	”	”	”	”	45
F_{41}(A–E)	XII_{12}–1	”	”	”	”	0	”	”	49
F_{42}(A–I)	XII_{13}–1	”	18	18	”	”	”	”	”
F_{46}(A–G)	XII_{17}–1	”	”	”	10	”	”	”	65
F_{45}(A–H)	XII_{16}–1	”	15	15	”	”	”	”	49
F_{47}(A–E)	XII_{18}–1	”	18	18	”	5	”	”	25
F_{48}(A–F)	XII_{19}–1	”	15	15	”	”	”	”	10

contained no B_2O_3, the activity was estimated as 34%, while in F_{39}(A)–F_{39}(I) series, 64%, and in F_{41}(A)–F_{41}(E), 49%, in both of which the catalyst contained 5% B_2O_3. Furthermore, in F_{45}(A)–F_{45}(H) and F_{49}(F) where the B_2O_3 content amounts to 10%, respectively, the activities have been observed to be 49% and 42%, respectively.

Therefore, we might say that the effect of B_2O_3 on Co+15% CeO_2+15%ThO_2+100% Kieselguhr catalyst is well detectable, as observed in Table 1; but as regards the suitable amount of B_2O_3, since 5% and 10% B_2O_3 give the effects practically to the same extent, it would be better to use a lesser amount of B_2O_3.

While in the presence of Cu, it has been observed that in the series of 18% CeO_2 and ThO_2, 10% B_2O_3 seemed to be better, but in the series of 15% CeO_2 and ThO_2, 5% B_2O_3 appeared to be better.

As regards the effect of Cu(6) on those series, shown in Table 3, regardless of the respective percentage of CeO_2, ThO_2, and B_2O_3, those catalysts without Cu seemed to give much higher activity.

The combined effects of ThO_2 and CeO_2, with or without Cu, in the presence of 10% B_2O_3, 18% series have been observed to be better, while in the presence of 5% B_2O_3, both 15% and 18% series appeared to be practically the same. As to the influence of Cu, here, also the negative effect is definitely shown, as already discussed in connection with Table 3.

Table 5 shows some of the typical results of the influences of pretreatment on the catalyst XII_{16}–1, Co+15% CeO_2+15% ThO_2+10% B_2O_3 +100% Kieselguhr, such as temperature and the duration of heat treatment prior to H_2 reduction and of temperature and the duration of H_2 reduction on the catalytic activity as measured by the average gas contractions.

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(6) (a) See also our report V, this Bulletin, **17** (1942), 252.
(b) Fischer, *Brenn-Chem.*, **11** (1930), 489, and the others mentioned in our Report V.
(c) S. Hamai, *J. Chem. Soc. Japan*, "Letter to the Editor" **63** (1942), 88

Table 5.

Effects of Pre-Treatments on the Catalysts

XII_{16}-1, $Co+15\%CeO_2+15\%ThO_2+10\%B_2O_3+100\%$Kieselguhr

Exp. No.	Heat Treatment Prior to H_2 Reduction (°C.)	(hrs.)	H_2 Reduction (°C.)	(hrs.)	Reaction Temp. (°C.)	Average Contraction (%)
F_{45}(A–H)	400	5	375	5	200	49
F_{49}(F)	"	"	"	"	"	42
F_{50}(A–J)	"	"	300	"	"	34
F_{51}(A–F)	"	"	400	"	"	15
F_{52}(A–H)	"	"	350	"	"	43
FC_7(A–D)	No heat treatment		"	10	"	64

Table 6 demonstrates the contraction percentage as affected by various factors. These results show clearly that whenever we speak of the catalytic activity, every influencing factor must be carefully mentioned, otherwise it is practically meaningless to speak of the catalytic activity.

Table 6.

Contraction percentage as affected by various factors.

Exp. No.	Catalyst No.	Catalyst Composition				Pre-Treatment				React. Temp.	Ave. Contraction
		Co+	ThO_2+	CeO_2+	Kieselguhr	Heat-treatment (°C.)	(hrs.)	Temp. at the Reduction Prior to Heating (°C.)	(hrs.)	(°C)	(%)
F_4	I_1-1	100	15	—	100	400	5	350	5	225	40
F_{14}	,,	,,	,,	—	,,	,,	2	,,	,,	,,	25
F_{34}(A–B)	XII_{13}-1	,,	—	15	,,	,,	5	375	,,	200	22
F_{10}	I_4-1	,,	18	—	,,	,,	4	350	,,	225	20
F_5	I_2-1	,,	20	—	,,	,,	2	,,	4	,,	70
F_{17}	,,	,,	,,	—	,,	,,	,,	,,	5	,,	15
F_{18}	,,	,,	,,	—	,,	,,	,,	,,	,,	,,	,,
F_{32}(A–E)	XII_{14}-1	,,	—	20	,,	,,	5	375	,,	200	35
F_6	I_3-1	,,	30	—	,,	,,	,,	350	2	225	70
F_{33}(A–D)	XII_{15}-1	,,	—	30	,,	,,	,,	375	5	200	24
F_{13}	I_8-1	,,	48	—	,,	,,	2	350	,,	225	60
F_{35}(A–D)	XII_8-1	,,	—	48	,,	,,	5	375	,,	200	17
F_9	I_5-1	,,	10	—	,,	,,	2	350	,,	225	6
F_{12}	,,	,,	,,	—	,,	,,	,,	,,	,,	,,	5
F_{31}(A–G)	XII_2-1	,,	—	10	,,	,,	5	,,	,,	200	54

Table 7 summarizes some of the possible correlations among the types of catalysts, their pre-treatments, the gas contraction percentage, oil yields, and gaseous products. As seen in this table, it cannot be so easily generalized that a parallelism between the gas contraction percentage and the oil yield, as evidenced by F_{49}(F), where the oil yield amounts to 171.7 c.c./m.^{3} with 42% contraction, while F_{39}(A–I) gives 121 c.c./m.^{3} with 64% contraction; F_{45}(A–H), 124.4 c.c./m.^{3} with 49% contraction, F_{46}(A–G), 127.1 c.c./m.^{3} with 65% contraction; and FC_7 (A–D), 129.4 c.c./m.^{3} with 64% contraction, respectively, although it

Table 7.

Exp. No.	Catalyst No.	Catalyst Composition (%)						Pre-treatment				Ave. Contraction (%)	Gaseous Products			Oil-yield cc/M³	Space Velocity
		Co	$+CeO_2$	$+ThO_2$	$+B_2O_3$	+ Kiesel guhr	+ Cu	Heat-treat. (°C.)	Heat-treat. (hrs.)	H_2 Reduction (°C.)	H_2 Reduction (hrs.)		CH_4 (%)	C_2H_6 (%)	Olefins (%)		
F_{39}(A–I)	XII_{12}–1	100	15	15	5	100	—	400	5	375	5	64	10	0.9	1.2	121	330
F_{40}(A–I)	XII_{11}–1	”	”	”	—	”	—	”	”	”	”	34	0	0	0.5	75	280
F_{41}(A–E)	XII_{12}–1	”	”	”	5	”	—	”	”	”	”	49	”	”	0.7	78	330
F_{42}(A–I)	XII_{13}–1	”	18	18	”	”	—	”	”	”	”	”	3.9	”	1.5	98	231
F_{43}(A–I)	XII_{14}–1	”	15	15	”	”	5	”	”	”	”	45	5.5	”	0.2	93.2	233
F_{44}(A–D)	XII_{15}–1	”	18	18	”	”	”	”	”	”	”	15	0	”	0.4	21.7	239
F_{45}(A–H)	XII_{16}–1	”	15	15	10	”	—	”	”	”	”	49	11.5	”	0.5	124.4	244
F_{46}(A–G)	XII_{17}–1	”	18	18	”	”	—	”	”	”	”	65	6.7	1.2	1.7	127.1	220
F_{47}(A–E)	XII_{18}–1	”	”	”	”	”	5	”	”	”	”	25	0	0	0.3	67.2	237
F_{48}(A–F)	XII_{19}–1	”	15	15	”	”	”	”	”	”	”	10	”	”	0.2	26.5	242
F_{49}(F)	XII_{16}–1	”	”	”	”	”	—	”	”	”	”	42	”	”	0.0	171.7	248
F_{50}(A–F)	”	”	”	”	”	”	—	”	”	300	”	34	—	—	—	95.1	246
F_{51}(A–F)	”	”	”	”	”	”	—	”	”	400	”	15	0	0	0.5	51.9	239
F_{52}(A–H)	”	”	”	”	”	”	—	”	”	350	”	43	3	2.4	0.7	63.1	242
FC_7(A–D)	”	”	”	”	”	”	—	—	—	”	10	64	16.2	1.1	1.6	129.4	”

(*) CH_4 formation tends to zero as time proceeds.

might be said that 50–65% gas contraction usually gives 120–130 c.c./m.^{3} in these series of catalysts.

Thus far we have tabulated some of the typical results of the investigations concerning the effects of promoters on the Co type catalyst, with respect to the gas contraction percentage as a measure of the catalytic activity, also with regard to the oil yield as well; and also we pointed out that the fundamental difficulty as to get a general statement concerning the gas contraction percentage as related to the oil yield—which is so far simply considered as somewhat parallel—but actually it is not so simple as expected. Some authors have just considered these problems as the simplest case, i.e., a parallelism exists between the gas contraction and the oil yield, regardless of the amount of gaseous products formed, such as CH_4, C_2H_6 or C_2H_4. It is quite evident that, whenever CH_4 formation predominates, the contraction percentage is enormously high and the oil yield is not so appreciable—usually, when CH_4 formation is very much appreciable, the oil yield is negligibly small, as we often pointed out(5) previously. Concerning suitable conditions for the synthesis of liquid hydrocarbons, it may probably be stated that the catalyst must be so rearranged that CH_4 formation is so restricted, or inhibited, as to direct the reaction of the liquid hydrocarbon synthesis on the catalytic surface, as required by our mechanism(7), previously discussed.

Summary.

(1) The effects on the Co type catalyst of such promoters as B_2O_3 and Cu, and the combined effects of ThO_2 and CeO_2 on the catalytic activity have been investigated and discussed.

(2) The effects of the pre-treatment on the catalytic activity have been investigated and discussed.

(3) It has been shown that there is a fundamental difficulty to generalize a parallel relationship between the gas contraction and the oil yields.

(4) In discussing the catalytic activity, that the CH_4 formation must be carefully segregated whenever we speak of the catalytic activity as to its oil forming ability has been pointed out as of paramount importance.

In conclusion, the author takes this occasion to express his 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; also he thanks to colleagues for their cooperation and to Messrs. Hayashi, Shimamura, Kuwabara, Igarashi and Fujiwara who have been willing to assist him in the experimental part of this investigation.

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(7) Report II, this Bulletin, **16** (1941), 213.