Physico-Chemical Investigations on Catalytic Mechanism. VIII. On the Fischer-Tropsch Synthesis of Hydrocarbons with Special Reference to the Durability of Catalyst. (Experimental Series II.) (4).

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Introduction. In a previous paper⁽¹⁾, we reported the experimental results relating to the durability and pretreatment of catalyst. In this paper we shall attempt to report some of our earlier experimental data for the durability of catalyst. We have been calling attention to the prime importance of durability of catalyst which may possibly depend on various factors, such as the method of preparation, history of pretreatment, constituents of the catalyst, as well as the type of promoters present and numerous others. For a systematic research for this type of investigation, the question of revivification is often taken up side by side, since the experimental investigation for the durability without revivification takes too much of the time although such data must be very essential, especially for developing a theory, as related to the catalytic activity and durability.

Here, in this paper we shall present some of our durability records for the catalyst I_1–1, Co+15%ThO_2+100% Kieselguhr and V_1–1, Co+12%U_3O_8+2.5%Cu+100%Kieselguhr. Preparations of the catalysts

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(1) Report VII, S. Hamai, *J. Chem. Soc. Japan*, **63**(1492), in press.

were similar to those already described in our earlier papers⁽²⁾. Experimental procedure was also analogous to those already mentioned in our previous papers. The catalyst I_1–1 and V_1–1 were pretreated by air at 400°C. for 2 hours prior to H_2 reduction at 350°C. for 5 hours, and after these pretreatments, the regular synthesis was proceeded by passing a $CO+H_2$ mixture ($CO:H_2=1:2$), 4 l./hr. at 225°C. The gas contraction percentage was taken as a measure of the activity, and the variation of the composition of the effluent gas was analyzed from time to time by using a modified form of the Orsat Gas Analysis Apparatus; in reality the gas samples were taken at the intervals of about 2 hours and analyzed.

Experimental Results and Discussions. Table 1 is more or less self explanatory. In Table 2, those gas analysis data for the effluent gas for F_4 in which the catalyst I_1–1, $CO+15\%ThO_2+100\%$Kieselguhr has been employed are shown. As seen in this table, after a certain period the synthesis reaction seemed to be normalized and in such a case more or less, no methane formation was observed⁽³⁾. In Table 3, those data for F_{14} for the same catalyst and similar pretreatment and experimental conditions are shown. Here we also noticed that after a certain period the

Table 1.

Exp. No.	Catalyst No.	Catalyst Comp.					Pretreatment				Exp. Durat.	React. Temp.	Cont. Percentage
							Heat. Treat.		H_2 Reduct.				
		Co	+ ThO_2	+ U_3O_8	+ Cu	+ Kies.	(°C.)	(hrs.)	(°C.)	(hrs.)	(hrs.)	(°C.)	(%)
F_4	1_1–1	100	15	—	—	100	400	2	350	5	65	225	40
F_{14}	"	"	"	—	—	"	"	"	"	"	"	"	15
F_{19}(A–K)	V_1–1	"	—	12	2.5	"	"	5	"	5	129⅔*	"	45–35
F_{19}(L)	"	"	—	"	"	"	—	—	270	2	6	190–250	70
F_{19}(M)	"	"	—	"	"	"	—	—	—	—	13	250	40
F_{19}**(N)	"	"	—	"	"	"	—	—	—	—	"	225	25
F_{19}(O)	"	"	—	"	"	"	—	—	—	—	10½	"	16
F_{19}(P)	"	"	—	"	"	"	—	—	300	2	4	225–300	22
F_{19}(Q)	"	"	—	"	"	"	400	2	270	5	13½	225	8
F_{19}(R)	"	"	—	"	"	"	—	—	—	—	12	230	44
F_{19}(S)	"	"	—	"	"	"	—	—	—	—	13	235	"

* Total hrs. for F_{19}(A–K)
** Rate of gas flow, 6–4 l./hr.

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(2) IV, this Bulletin, **17**(1942), 166.
V, this Bulletin, **17**(1942), 252.
VI, this Bulletin, **17**(1942), 339.

(3) Samples 22, 24 and 28 show a few percent of CH_4; this is probably due to the local variation of reaction temperature on the particular part of the catalyst which might possibly have caused the CH_4 formation (i.e., temperature rises locally owing to the possible fluctuation of the gas flow which in turn causes the insufficient conducting of the heat.).

Table 2.

(F_{14}) Catalyst I_1–1, Co+15% ThO_2+100% Kieselguhr.
Heat treatment prior to H_2 Reduction, 400°C., 2 hrs.
H_2 Reduction, 350°C., 5 hrs.
Duration of Experiment, 65 hrs.
Reaction temperature, 225°C.
Rate of Gas Flow, 4 l./hr., $CO:H_2=1:2$.

Gas Analysis Data

Sample No.	1	2	3	4	5	6	7	8	9	10	11
CO_2	0.1	0.2	5.0	12.7	7.0	4.2	2.5	2.0	2.6	2.6	2.5
C_2H_2	0.0	0.0	0.0	0.2	0.3	0.0	0.3	0.0	0.7	0.3	0.0
C_2H_4	0.3	0.2	0.0	0.3	0.8	0.7	0.5	1.0	0.7	0.4	0.5
C_nH_{2n}	0.0	0.3	0.2	0.2	0.2	0.5	0.7	0.2	0.0	0.8	0.4
O_2	0.6	0.4	0.3	0.4	0.4	0.6	1.0	0.3	0.4	0.3	0.6
CO	14.8	20.5	14.1	7.6	16.4	21.1	25.6	26.5	25.6	26.7	28.5
H_2	81.3	76.9	70.0	56.8	62.9	64.1	64.0	65.4	64.8	64.1	64.7
CH_4	0.0	0.0	6.5	19.2	8.0	5.6	0.0	2.7	3.0	2.8	0.0
C_2H_6	0.0	0.0	0.0	0.6	2.2	0.9	0.0	0.0	0.0	0.0	0.0
N_2	2.9	1.5	3.9	2.0	1.8	2.3	4.5	1.9	2.3	2.1	2.8

Sample No.	12	13	14	15	16	17	18	19	20	21	22
CO_2	3.0	1.1	0.6	0.4	0.0	1.0	1.3	1.0	1.1	0.0	1.1
C_2H_2	0.4	0.2	0.0	0.2	0.0	0.3	0.3	0.2	0.4	0.6	0.3
C_2H_4	0.6	0.5	0.5	0.8	0.5	0.2	0.4	0.3	0.5	0.3	0.3
C_nH_{2n}	0.3	0.2	0.4	0.6	0.2	0.5	0.2	0.5	0.5	0.2	0.2
O_2	0.4	0.5	0.3	0.3	0.4	0.4	0.3	0.4	0.2	0.7	0.2
CO	27.5	30.3	30.9	28.7	30.2	27.1	30.3	30.4	30.4	31.2	30.9
H_2	61.9	65.1	65.7	66.2	66.8	68.4	65.5	65.3	65.8	64.4	64.8
CH_4	3.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.9
C_2H_6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N_2	2.4	2.1	1.6	1.8	1.9	2.1	1.7	1.9	1.1	2.6	1.4

Sample No.	23	24	25	26	27	28	29	30	31*
CO_2	1.1	1.4	1.2	1.3	1.1	1.4	1.2	1.1	0.0
C_2H_2	0.4	0.0	0.2	0.5	0.2	0.3	0.1	0.3	0.0
C_2H_4	0.5	0.6	0.6	0.7	0.7	0.5	0.7	0.4	0.0
C_nH_{2n}	0.2	0.0	0.2	0.1	0.4	0.2	0.5	0.2	0.0
O_2	1.4	0.4	0.3	0.3	0.3	0.4	0.5	0.4	0.3
CO	26.4	27.1	29.7	28.9	30.1	26.1	29.0	30.6	30.7
H_2	63.9	67.4	65.9	66.6	65.6	68.4	65.9	65.5	67.6
CH_4	0.0	0.8	0.0	0.0	0.0	0.4	0.0	0.0	0.0
C_2H_6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N_2	6.1	2.3	1.9	1.6	1.6	2.2	2.1	1.5	1.4

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* Initial Gas Mixture.

Table 3.

(F_{14}) Catalyst I_1–1, Co+15%ThO_2+100% Kieselguhr.
Heat Treatment prior to H_2 Reduction, 400°C., 2 hrs.
H_2 Reduction, 350°C., 5 hrs.
Duration of Experiment, 65 hrs.
Reaction Temperature, 225°C.
Rate of Gas Flow, 4 l./hr., $CO:H_2=1:2$.

Gas Analysis Data

Sample No.	1	2	3	4	5	6	7	8	9	10	11
CO_2	0.0	0.2	2.4	2.0	0.4	0.8	0.6	0.5	0.7	0.3	0.4
C_2H_2	0.2	0.2	0.2	0.3	0.6	0.2	0.1	0.3	0.2	0.3	0.3
C_2H_4	0.0	0.0	0.4	0.3	0.4	0.5	0.3	0.2	0.3	0.7	0.5
C_nH_{2n}	0.0	0.1	0.5	0.2	0.0	0.0	0.0	0.0	0.2	0.0	0.0
O_2	0.4	0.3	0.4	0.5	0.3	0.4	0.4	0.3	0.5	0.4	0.4
CO	0.0	0.0	18.5	23.7	30.3	31.2	31.6	32.6	31.1	31.3	31.4
H_2	97.9	86.2	67.6	70.2	66.1	65.1	65.1	65.5	64.9	65.2	65.1
CH_4	0.0	10.5	7.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C_2H_6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N_2	1.5	2.5	2.1	2.8	1.9	1.8	1.9	1.6	2.1	1.8	1.9

Sample No.	12	13	14	15	16	17	18	19	20	21	22
CO_2	0.2	0.4	0.4	0.6	0.2	0.3	0.3	1.2	0.8	1.1	0.5
C_2H_2	0.2	0.2	0.3	0.3	0.3	0.0	0.2	0.1	0.3	0.0	0.2
C_2H_4	0.3	0.3	0.3	0.2	0.2	0.5	0.3	0.0	0.4	0.7	0.3
C_nN_{2n}	0.0	0.0	0.0	0.0	0.3	0.2	0.0	0.0	0.3	0.2	0.1
O_2	0.2	0.3	0.4	0.3	0.2	0.5	0.3	0.2	0.3	0.6	0.4
CO	32.3	31.8	31.5	31.1	31.1	30.7	30.4	30.6	29.2	29.0	29.6
H_2	65.1	65.6	65.4	65.9	66.4	65.4	66.7	66.5	67.0	65.7	66.9
CH_4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C_2H_6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N_2	1.2	1.4	1.7	1.6	1.3	2.4	1.8	1.4	1.7	2.7	2.0

Sample No.	23	24	25	26	27	28	29	30	31	32	33
CO_2	0.6	0.5	0.3	0.0	0.4	0.6	0.2	0.4	0.3	0.3	0.4
C_2H_2	0.0	0.1	0.1	0.2	0.3	0.2	0.3	0.3	0.3	0.2	0.3
C_2H_4	0.1	0.5	0.0	0.4	0.2	0.3	0.2	0.2	0.0	0.3	0.2
C_nH_{2n}	0.3	0.3	0.4	0.2	0.2	0.2	0.3	0.0	0.2	0.0	0.1
O_2	0.2	0.3	0.3	0.2	0.3	0.4	0.3	0.5	0.3	0.4	0.2
CO	30.5	26.0	26.1	31.7	33.0	31.3	31.6	31.3	32.3	32.4	33.8
H_2	67.0	70.7	71.5	66.2	64.4	64.3	65.9	65.1	65.3	64.7	64.0
CH_4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C_2H_6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N_2	1.3	1.6	1.3	1.1	1.2	1.7	1.5	2.2	1.3	1.7	1.0

synthesis reaction was definitely normalized so that no CH_4 formation was observed as long as the catalyst surface remained suitable to the normalized reaction. We noticed almost without exception that the formation of C_2H_4 was observed and furthermore C_2H_4 percentages seemed to be, more or less, about the same. This very fact is consistent with the view already discussed⁽⁴⁾ that the role played by CH_2 during the normal synthesis of the Fischer-Tropsch reaction is no longer doubtful, as it is evidenced by

Table 4.

F_{19}–(A–K) Catalyst V_1–1.
$Co+12\%U_3O_8+2.5\%Cu+100\%$ Kieselguhr.
Heat Treatment Prior to H_2 Reduction, 400°C., 5 hrs.
H_2 Reduction, 350°C., 5 hrs.
Space Velocity 342.
Reaction Temperature 225°C.
Duration of Experiment, 19 days F_{19}–(A–S).
Oil Yield 180 cc./m^3.
Rate of Gas Flow 4 l./hr., $CO:H_2=1:2$.

Exp. No.	Exp. Duration (hrs.)	Ave. Gas Contraction (%)	Remarks
F_{19}–A	6	45	Oil Yields 180 c.c./m.^{3} (A–E)
F_{19}–B	12	45	
F_{19}–C	12	40	
F_{19}–D	12	40	
F_{19}–E	13	40	
F_{19}–F	13	35	
F_{19}–G	12	35	
F_{19}–H	11$^2/_3$	30	Oil Yields 100–80 c.c./m^3 (F–K)
F_{19}–I	13	35	
F_{19}–J	13	35	
F_{19}–K	12	35	
F_{19}–L	6	70	Reduction at 270°C. by H_2 for 2 hrs. Reaction at 190°–250°C.
F_{19}–M	13	40	Reaction at 250°C.
F_{19}–N	13	25	Reaction at 225°C. Rate of Gas Flow 6–4 l./hr.
F_{19}–O	10½	16	Reaction at 225°C.
F_{19}–P	4	22	Reaction at 225°–300°C. After Rereduction at 300C. for 2 hrs.
F_{19}–Q (225°C.)	13½	8	Heat Treatment at 400°C for 2 hrs. H_2 Reduction at 270°C for 5 hrs.
F_{19}–R (230°C.)	12	44	
F_{19}–S (235°C.)	13	44	

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(4) S. Hamai, this Bulletin, **16** (1941), 213.

various accumulated facts in hydrocarbon chemistry in general⁽⁵⁾, and starting from CH_2, if polymerized to C_2H_4, various reactions, including polymerization and hydrogenation, leading to higher hydrocarbons are quite easily attained, as pointed out by Egloff, Schaad and Lowry⁽⁶⁾, furthermore, Egloff and Wilson⁽⁷⁾ pointed out that C_2H_4 acts as the key substance in hydrocarbon chemistry, in other words, the reaction $-\text{Co}-\overset{CH_2}{\overset{|}{\text{Co}}}-\text{Co}- \rightarrow -\text{Co}-\overset{C_2H_4}{\overset{|}{\text{Co}}}-\text{Co}-$, is faster than the reaction $-\text{Co}-\overset{CH_2}{\overset{|}{\text{Co}}}-\text{Co}- \rightarrow -\text{Co}-\overset{CH_4}{\overset{|}{\text{Co}}}-\text{Co}-$ in the normalized reaction, while the formation of CH_4 at the initial stage predominates via different paths and its formation is faster at the initial stage,⁽⁸⁾ and as the reaction becomes normalized the reaction of CH_4 formation at the initial stage must be restricted, or prohibited, as we have already pointed out⁽⁹⁾.

In Table 4, the results for the catalyst V_1–1, Co+12% U_3O_8+2.5% Cu +100% Kieselguhr, are shown. Pretreatment by air at 400°C. for 5 hours and H_2 reduction at 350°C. for 5 hours and the reaction was proceeded at 4 l./hr. and 225°C. and various other conditions are indicated in the table. Here we tabulated experimental duration, average gas contraction percentages and oil yields. Table 5 gives the gas analysis data for F_{19}–A—F_{19}–K. Here also we noticed that the methane formation at the initial stage and C_2H_4 formation in every gas sample are consistent with the explanation already mentioned. Table 6 is for F_{19}–L, where the catalyst was rereduced by H_2 at 270°C. for 2 hours then it proceeded the regular synthesis at 190–250°C. When the reaction temperature was as

Table 5. Gas Analysis Data.

F_{19}-(A-K)

Exp. No.	F_{19}-A	F_{19}-B	F_{19}-C	F_{19}-D	F_{19}-E	F_{19}-F	F_{19}-G	F_{19}-H	F_{19}-I	F_{19}-J	F_{19}-K
CO_2	2.3	0.3	1.0	1.5	0.8	0.7	1.1	0.7	0.8	0.8	0.8
C_2H_2	0.3	0.0	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C_2H_4	0.4	0.3	0.7	1.1	1.6	0.5	0.6	0.4	0.9	1.0	1.1
C_nH_{2n}	0.0	0.4	0.0	0.0	0.2	0.0	0.3	0.0	0.0	0.0	0.0
O_2	0.5	0.4	0.3	0.5	0.3	0.5	0.4	0.3	0.4	0.3	0.3
CO	20.5	30.2	29.5	30.4	30.9	30.3	31.8	30.6	30.6	30.7	31.2
H_2	69.0	66.0	66.6	63.9	64.7	65.8	64.1	66.4	65.5	65.8	65.2
CH_4	6.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C_2H_6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N_2	2.5	1.9	1.4	2.7	1.5	2.2	1.7	1.6	1.7	1.4	1.4

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(5) (a) R. G. W. Norrish, *Proc. Roy. Soc.* (London), A **150**(1925), 36.
(b) L. S. Kassel, *J. Am. Chem. Soc.*, **54**(1932), 3949.
(c) L. E. H. Bawn, *Trans. Faraday Soc.*, **34**(1938), 598.
(d) D. E. W. R. Steacie, *Chem. Rev.*, **22**(1938), 311.

(6) Egloff, Schaad and Lowry, *J. Phys. Chem.*, **35**(1931), 1825.

(7) Egloff and Wilson, *Ind. Eng. Chem.*, **27**(1935), 917.

(8) S. Hamai, S. Hayashi and K. Shimamura, this Bulletin, **17**(1942), 252.

(9) S. Hamai, this Bulletin, **16**(1941), 213.

Table 6. Gas Analysis Data.

F_{19}–L, Re-reduction by H_2 at 270°C., for 2 hrs.

Reaction Temp. (°C.)	190	190	225	250	250
Sample No.	1	2	3	4	5
CO_2	0.2	0.4	0.0	9.2	13.6
C_2H_2	0.0	0.0	0.0	0.0	0.2
C_2H_4	0.0	0.0	0.4	0.5	0.2
C_nH_{2n}	0.0	0.0	0.0	0.0	0.0
O_2	0.7	0.4	0.3	0.5	0.4
CO	7.1	27.2	30.7	17.8	12.1
H_2	89.1	70.2	67.2	57.7	57.0
CH_4	0.0	0.0	0.0	12.0	14.6
C_2H_6	0.0	0.0	0.0	0.0	0.0
N_2	2.9	1.8	1.4	2.3	1.9

high as 250°C., there we found difinitely the formation of CH_4—also C_2H_4 formation. Table 7 shows the gas analysis data for F_{19}–M where the same catalyst as F_{19}–L was used but only the reaction temperature was varied 250–240°C. The formation of methane decreases distinctly with the decrease of the reaction temperature, as seen in the table. Table 8 shows the data of gas analyses for F_{19}–N where the reaction was proceeded at 225°C.; here again we observed that at the initial stage CH_4 was found, and as the reaction was normalized, the formation of CH_4 was completely restricted, while without exception C_2H_4 was observed.

Table 7. Gas Analysis Data.

F_{19}–M Continued from F_{19}–L

Reaction Temp. (°C.)	250	250	250	250	240	240	240
Sample No.	1	2	3	4	5	6	7
CO_2	12.0	14.1	14.8	10.5	3.3	2.6	3.0
C_2H_2	0.2	0.2	0.2	0.0	0.0	0.0	0.0
C_2H_4	0.5	0.6	0.3	0.5	0.9	1.2	1.3
C_nH_{2n}	0.0	0.0	0.0	0.0	0.3	0.0	0.0
O_2	0.3	0.3	0.4	0.5	0.4	0.3	0.4
CO	11.7	4.6	2.5	7.5	22.1	25.9	26.1
H_2	51.8	52.2	57.9	57.9	65.2	64.6	63.5
CH_4	18.5	25.1	18.2	17.8	4.5	2.8	3.8
C_2H_6	2.6	0.0	4.0	3.2	1.4	1.2	0.5
N_2	1.3	1.9	1.8	2.1	1.9	1.4	1.7

Table 8. Gas Analysis Data.

F_{19}–N Continued from F_{19}–M

Reaction Temp. (°C.)	225	225	225	225	225	225	225
Sample No.	1	2	3	4	5	6	7
CO_2	4.2	0.6	0.4	0.5	0.6	0.6	0.4
C_2H_2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C_2H_4	1.2	0.8	0.5	0.6	0.9	0.7	0.5
C_nH_{2n}	0.3	0.0	0.0	0.2	0.0	0.0	0.0
O_2	0.3	0.3	0.5	0.4	0.4	0.3	0.5
CO	24.3	29.3	30.3	29.4	30.0	28.2	29.3
H_2	59.4	66.9	66.0	67.1	66.1	69.5	67.0
CH_4	8.9	0.0	0.0	0.0	0.0	0.0	0.0
C_2H_6	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N_2	1.7	2.1	2.3	1.8	2.0	1.6	2.3

Table 9 shows the data for F_{19}–0. Here again we confirmed the methane formation at 270°C. and no CH_4 formation at 225°C.. Table 10 indicates the data for F_{19}–P where the catalyst was re-reduced at 300°C. for 2 hours by H_2 and the reaction was proceeded at 225°C.. Table 11 gives the data for F_{19}–Q where the same catalyst was pretreated by air at 400°C. for 2 hours and re-reduced by H_2 at 270°C. for 5 hours and then the reaction at 225°C.. Here also we see that during a certain initial period CH_4 formation was observed then it became null after the reaction

Table 9. Gas Analysis Data.

F_{19}–O Continued from F_{19}–N

Reaction Temp. (°C.)		270	225	225	225	225	225
Sample No.	1	2	3	4	5	6	7
CO_2	2.4	12.8	1.1	0.5	0.6	0.5	0.5
C_2H_2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C_2H_4	0.6	1.0	0.5	0.9	0.7	0.3	0.4
C_nH_{2n}	0.0	0.0	0.0	0.0	0.2	0.0	0.0
O_2	0.5	0.3	0.3	0.4	0.3	0.4	0.3
CO	28.0	7.7	29.2	28.4	29.2	29.0	30.2
H_2	66.2	59.0	67.2	67.4	67.6	68.1	66.9
CH_4	0.0	14.4	0.0	0.0	0.0	0.0	0.0
C_2H_6	0.0	1.7	0.0	0.0	0.0	0.0	0.0
N_2	2.3	1.8	1.7	2.4	1.4	1.7	1.6

Table 10. Gas Analysis Data.

F_{19}-P Re-reduction at 300°C. for 2 hrs. by H_2

Reaction Temp. (°C.)	225	225	225	225
Sample No.	1	2	3	4
CO_2	0.0	0.2	0.4	0.6
C_2H_2	0.0	0.0	0.0	0.0
C_2H_4	0.0	0.4	0.6	0.7
C_nH_{2n}	0.0	0.0	0.0	0.0
O_2	0.4	0.3	0.4	0.5
CO	0.0	0.7	24.6	28.2
H_2	97.5	69.9	72.1	67.9
CH_4	0.0	0.0	0.0	0.0
C_2H_6	0.0	0.0	0.0	0.0
N_2	2.1	1.7	1.9	2.1

Table 11. Gas Analysis Data.

F_{19}-Q, Heat treatment at 400°C. for 2 hrs.
Re-reduction at 270°C. for 5 hrs. by H_2.

Reaction Temp. (°C.)	225	225	225	225	225	225	225
Sample No.	1	2	3	4	5	6	7
CO_2	0.2	4.0	2.0	0.9	0.5	0.5	0.4
H_2H_2	0.0	0.0	0.2	0.0	0.0	0.0	0.0
C_2H_4	0.2	0.3	0.3	0.5	0.5	0.6	0.6
C_nH_{2n}	0.0	0.0	0.0	0.0	0.0	0.2	0.2
O_2	0.6	0.3	0.4	0.4	0.4	0.3	0.4
CO	0.0	2.8	24.3	29.4	30.1	30.7	29.4
H_2	96.3	75.0	62.7	66.9	66.5	66.2	66.9
CH_4	0.0	14.6	7.7	0.0	0.0	0.0	0.0
C_2H_6	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N_2	2.7	2.1	1.9	1.8	2.0	1.5	2.1

attained so-called normalized condition. Table 12–13 indicate the data for the reaction temperatures 230°–235°C., respectively. Here once again, as far as the CH_4 formation and C_2H_4 formation are concerned, they are no exceptional cases, as already stated before. As seen in these data, the fact that the CH_4 formation predominates at the higher reaction temperature is probably due to the circumstance that the formation of CH_4 becomes faster and of comparable order with the normalized synthesis reaction. (Within the tested temperature ranges).

Table 12. Gas Analysis Data.

F_{19}-R (Continued from F_{19}-Q)

Reaction Temp. (°C.)	230	230	230	230	230	230	230
Sample No.	1	2	3	4	5	6	7
CO_2	0.5	3.0	2.7	1.6	1.1	0.7	1.0
C_2H_2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C_2H_4	0.8	0.7	1.0	1.1	0.9	0.5	0.9
C_nH_{2n}	0.2	0.3	0.3	0.3	0.0	0.2	0.0
O_2	0.5	0.3	0.4	0.4	0.4	0.5	0.4
CO	30.2	26.2	26.9	28.9	29.6	29.9	29.4
H_2	65.4	61.1	61.7	61.7	66.2	66.0	66.2
CH_4	0.0	7.1	5.3	4.4	0.0	0.0	0.0
C_2H_6	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N_2	2.4	1.3	1.7	1.6	1.8	2.2	2.1

Table 13. Gas Analysis Data.

F_{19}-S (Continued from F_{19}-R)

Reaction Temp. (°C.)	235	235	235	235	235	235	235	235
Sample No.	1	2	3	4	5	6	7	8
CO_2	0.9	3.7	4.4	2.8	2.5	2.6	1.6	1.2
C_2H_2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C_2H_4	1.1	1.2	0.9	0.9	0.8	0.8	0.6	0.7
C_nH_{2n}	0.2	0.0	0.4	0.3	0.3	0.4	0.2	0.0
C_2	0.5	0.3	0.4	0.4	0.3	0.6	0.4	0.3
CO	27.3	26.1	25.6	27.6	27.4	25.5	28.7	29.5
H_2	67.8	60.7	58.5	62.2	63.7	61.1	66.3	66.8
CH_4	0.0	6.3	7.9	2.9	3.8	5.6	0.0	0.0
C_2H_6	0.0	0.0	0.0	1.1	0.0	0.0	0.0	0.0
N_2	2.2	1.7	1.9	1.8	1.2	2.4	2.2	1.5

Thus, we have demonstrated rather conclusively that the formation of CH_4 at the initial stage predominates and it gradually becomes null as the reaction surface is normalized, and these have been tested with various different pretreatments as well as different reaction temperatures. Furthermore, we also have shown that as the reaction temperature becomes higher the CH_4 formation definitely tends to become appreciable; and without exception, the C_2H_4 formation, with a fairly constant amount, can be observed even with the catalyst composition differing and with various different pretreatments.

Summary.

(1) The durability experiments with the catalysts, Co+15%ThO_2+100%Kieselguhr and Co+12%U_3O_8+2.5%Cu+100%Kieselguhr, are reported and tabulated.

(2) Following mainly the gas analysis data, the normalized reaction was discussed with special reference to the initial formation of CH_4.

(3) Some correlations with the formation of C_2H_4, in connection with our reaction mechanism already proposed, as well as the predominating tendency of CH_4 formation at higher reaction temperature have been given.

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