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Studies of the Fischer–Tropsch Synthesis. V. Activities and Surface Areas of Reduced and Carburized Cobalt Catalysts[1]

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Introduction

Although the Fischer–Tropsch synthesis has been studied for more than twenty years, Craxford[3,4,5] was the first to attempt to relate activity and product distribution to the nature of the catalyst surface and the adsorbed layer of hydrocarbons upon it. Recently Hofer,[6,7] Weller,[8,9] Anderson[1,10–12] and Storch[13] have presented kinetic studies, X-ray diffraction data and surface area and pore volume studies of cobalt catalysts, and Pichler[14] has prepared a critical summary of the data of German research pertaining to the Fischer–Tropsch synthesis in which many of these factors are considered. The present paper relates surface area and surface accessibility to activity and product distribution. The data reported previously on the effect of bulk carbide on the activity of cobalt catalysts[9] have been extended to include the surface areas, activities and distribution of products in the synthesis with catalysts carburized with carbon monoxide under conditions which form carbide (Co_2C), "free" carbon or both.

Experimental

The catalysts studied in this paper were Co:ThO$_2$:MgO:kieselguhr (100:6:12:200) catalysts characterized as number 89 and Co:ThO$_2$:kieselguhr (100:18:100) catalyst number 108 B. Descriptions have been published of the preparation and testing of these catalysts[10,11,13] as well as their surface areas,[1,11] mercury and helium densities[1,11] and activities at 185°.[12] In all tests described in this paper approximately two volumes of hydrogen to one volume of carbon monoxide synthesis gas was used. Surface areas were determined from adsorption isotherms of nitrogen at $-195°$ by the simple equation of Brunauer, Emmett and Teller.[15] The method of determination of the volume of chemisorbed carbon monoxide at $-195°$ has been described previously.[1]

Surface areas and mercury and helium densities were determined on a catalyst removed from a converter during the twelfth week of operation. The catalyst was dropped from the converter in an atmosphere of synthesis gas and at synthesis temperature into a tube through which pure argon was flowing. This tube was joined to the bottom of the converter by a rubber sleeve in which there was a small hole to allow the argon and synthesis gas to escape. When the catalyst had cooled to room temperature, it was transferred in a stream of carbon dioxide to suitable adsorption and density tubes. In this method of transfer, there was no possibility of exposure of the catalyst to air.

In the carburization studies reduced catalysts were treated with pure carbon monoxide prepared by dehydration of formic acid in the presence of phosphoric acid.[16] For surface area determinations, the catalyst was carburized in a glass adsorption tube[17] in a small automatically controlled electric furnace. For tests of carburized catalysts in the synthesis, the samples were treated with carbon monoxide in the converter. Before carburization, the catalyst that had been used in the synthesis was treated with hydrogen at 208° to remove most of the adsorbed hydrocarbons.

In many instances in this paper the results from cobalt–thoria–kieselguhr and cobalt–thoria–magnesia–kieselguhr catalysts have been compared as though the catalysts were the same. This is permissible since it has been found that the distribution of products, dependencies of rate upon temperature and pressure and the behavior of catalysts during and after carburization were very similar for these two types of catalysts.

Surface Areas and Pore Volumes of Catalysts Used in the Synthesis

Pelleted catalyst 89FF (Co–ThO$_2$–MgO–kieselguhr) was removed from the converter during the twelfth week of operation at atmospheric pressure and transferred to suitable adsorption and density tubes in a manner that precluded exposure to air. The catalyst had been operated at an average temperature of 183° for eleven weekly periods of five days each with a two-hour reactivation in hydrogen at 195° followed by a forty-four-hour period in which a very slow stream of hydrogen was passed over the catalyst at about 150° between operating periods. Although the activity decreased somewhat during each period, the average activity of each period was the same for all eleven weeks. When removed from the converter, the catalyst had been operated for four days in the twelfth week. Since as indicated in Table I about 90% of the hydrocarbons on the catalyst should be removed by hydrogenation at 195°, most of the hydrocarbon on the catalyst was formed in the four days of operation prior to its transfer. Data of adsorption and mercury and helium densities are given in Tables I and II.

After use in the synthesis, the area of the catalyst was 4.36 square meters per gram compared with 80.0 square meters per gram after the initial reduction. The hydrogen reactivation at 200° for two hours decreased the weight of the sample by 23.5% and increased the surface area to 70.5 square meters per gram. Further reduction at 200° for twenty hours produced only a slight loss in weight and a small increase in area. Reduction at 400° under conditions of the original reduction of the catalyst caused only a slight loss in weight and increased the area to nearly that

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[1] Part IV of this series Anderson, Hall and Hofer, THIS JOURNAL, **70**, 2465 (1948).

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(3) Craxford and Rideal, *J. Chem. Soc.*, 1604 (1939).

(4) Craxford, *Trans. Faraday Soc.*, **42**, 580 (1946).

(5) Craxford, *Fuel in Sci. and Practice*, **26**, 119 (1947).

(6) Hofer and Peebles, THIS JOURNAL, **69**, 2497 (1947).

(7) Hofer and Peebles, *ibid.*, to be published.

(8) Weller, *ibid.*, **69**, 2432 (1947).

(9) Weller, Hofer and Anderson, *ibid.*, **70**, 799 (1948).

(10) Anderson, Krieg, Seligman and O'Neill, *Ind. Eng. Chem.*, **39**, 1548 (1947).

(11) Anderson, Hall, Hewlett and Seligman, THIS JOURNAL, **69**, 3114 (1947).

(12) Anderson, Krieg, Seligman and Tarn, *Ind. Eng. Chem.*, in press.

(13) Storch, *et al.*, Bureau of Mines Technical Paper 709, "Synthetic Liquid Fuel Process. Hydrogenation of Carbon Monoxide," Part I, 1948.

(14) Pichler, "Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen," Bureau of Mines, Special Report, 1947.

(15) Brunauer, Emmett and Teller, THIS JOURNAL, **60**, 309 (1938).

(16) Thompson, *Ind. Eng. Chem.*, , 389 (1929).

(17) Anderson, *Ind. Eng. Chem.*, *Anal. Ed.*, **18**, 156 (1946).

TABLE I

ADSORPTION DATA FOR REDUCED AND USED COBALT CATALYST 89FF[a]

All adsorption data per gram of unreduced catalyst

Treatment	Cumulative weight loss, %[b]	Surface area, sq. m./g.	V_m,[c] cc./g.	V_{CO},[d] cc./g.	V_{CO}/V_m
a. Reduced 2 hr. of H_2 at 400°, SVH = 6000[e]	.	80.8	18.45	3.2	0.173
b. Used (a) plus 12 weeks of synthesis	0.0	4.36	1.00	0.13	.130
c. (b) plus 2 hr. of H_2 at 200°, SVH = 200	23.5	70.5	16.1	2.7	.168
d. (c) plus 20 hr. of H_2 at 200°, SVH = 200	23.7	74.2	16.9	3.2	.189
e. (d) plus 2 hr. of H_2 at 400°, SVH = 6000	25.3	79.1	18.1	3.8	.210

[a] Cobalt:thoria:magnesia:kieselguhr = 100:6:12:200. [b] Weight based on weight of used catalyst as removed from converter. [c] Volume of nitrogen corresponding to a physically adsorbed monolayer. [d] Volume of carbon monoxide chemisorbed at −195°. [e] Space velocity per hour, volumes of gas (S.T.P.) per volume of catalyst per hour.

TABLE II

DENSITY AND PORE VOLUME DATA ON REDUCED AND USED COBALT CATALYST 89FF[a]

Treatment	Cumulative weight[b] loss, %	d_{He} g./cc.	d_{Hg}, g./cc.	Pore volume, cc./g.
a. Reduced 2 hr. at H_2 at 400° SVH[c] = 6000	..	3.031	1.138	0.549[d]
b. Used (a) plus 12 weeks of synthesis	0.0	1.891	1.471	0.151[e] (0.201)[d]
c. (b) plus 2 hr. of H_2 at 200°, SVH = 200	23.8	2.881	...	.....
d. (c) plus 2 hrs. of H_2 at 400°, SVH = 6000	25.5	3.007	1.112	0.566[d]

[a] Cobalt:thoria:magnesia:kieselguhr = 100:6:12:200. [b] Weight was based on weight of used catalyst as removed from converter. [c] Space velocity per hour, volumes of gas (S.T.P.) per volume of catalyst per hour. [d] Pore volume in cc. per gram of reduced catalyst. [e] Pore volume in cc. per gram of catalyst as removed from converter.

of the original reduced catalyst. The ratio of volume of chemisorbed carbon monoxide to V_m[18] for nitrogen varied from 0.13 to 0.21, the ratio increasing with increasing surface area of the sample. It is interesting to note that even on the catalyst removed from the converter some cobalt was accessible to chemisorb carbon monoxide.

The helium density of the used catalyst was 1.891 and after reduction at 400°, 3.007, which is nearly equal to that of the original reduced catalyst. The mercury density of the used catalyst decreased on reduction at 400° from 1.471 to 1.112, while the pore volume (volume of pores with openings smaller than 5 microns in diameter[1,19]) increased from 0.201 to 0.566 cc. per gram of unreduced catalyst. Thus, the surface area, densities and pore volume of the used catalyst after reduction at 400° were very nearly identical to those of the original reduced catalyst.

The volumes of mercury displaced by the used catalyst before and after reduction per unit weight of cobalt were identical, indicating that the adsorbed hydrocarbons were located within the pellet in the space not penetrated by mercury and not on the external surface of the catalyst. At 30°, 65% of the pore volume of the used catalyst was filled with hydrocarbons. The hydrocarbons removed by hydrogenation had a density of 0.90 as calculated from change in weight and change in volume of helium displaced. This density compares well with the densities of soft and hard paraffins from atmospheric pressure synthesis, 0.90 and 0.93, respectively, as reported by Pichler.[14]

The data in Tables I and II establish definitely that the catalyst in its normal condition of operation at atmospheric pressure is heavily covered with hydrocarbons. In pressure operation, the catalyst is believed to be completely filled with hydrocarbon product at all times.[5] Experiments given in Table III indicate that the activities[20] of pelleted cobalt catalysts at one atmosphere are equal or slightly greater than at 7.8 atmospheres operating pressure. Pelleted catalysts produced greater percentages of methane and light hydrocarbons at 7.8 atmospheres than at one atmosphere, but granular catalysts produced nearly the same products under both conditions.

At atmospheric pressure, it was found that the percentage of methane and light hydrocarbons increased with increasing mercury density of the catalyst.[12] It was also found that granular and pelleted forms of the same catalyst had the same activity per gram of catalyst.[12] At 7.8 atmospheres a pelleted catalyst of higher density and greater pellet size had a lower activity and formed greater amounts of light hydrocarbons than a less dense and smaller size pelleted catalyst as shown in Table IV. Thus the larger pellets in test X-58 at a 4° higher temperature than in X-45 produced less oil than the smaller pellets, even though a greater weight of catalyst was used in X-58.

In Table V, data are presented for a test of a pelleted catalyst operated alternately at 1 and 7.8 atmospheres. After six weekly periods of operation at atmospheric pressure, the catalyst was operated at 7.8 atmospheres. No change in activity was observed. After a hydrogen reactivation, operation at one atmosphere required a 5° higher temperature to produce the same degree of conversion. After hydrogen reactivation, it was possible to operate at 7.8 atmospheres at 3° lower than in the previous period (h). In week j, operation at one atmosphere without a hydrogen reactivation required a temperature 10° higher than in the week i. Subsequent operation at 7.8 atmospheres after hydrogen reactivation was possible at the same temperature as in week j. Operation at one atmosphere in week 1 without reactivation required a 21° higher temperature than in week f.

Thus, operation at 7.8 atmospheres decreased the activity at atmospheric pressure. When hydrogen reactivation was omitted, the decrease in activity at atmospheric pressure operation after a period at 7.8 atmospheres was greater. In addition to changes in activity, alternation of operation at 1 and 7.8 atmospheres increased the percentage of methane and light hydrocarbons in the products compared with previous periods of operation at 1 and 7.8 atmospheres, respectively.

Surface Areas and Activities of Carburized Cobalt Catalysts

Studies were made of the surface areas and activities (at atmospheric pressure) of pelleted Co–ThO_2–kieselguhr catalyst 108B after carburization at 208, 235 and 275°. Hofer[6,7] has shown that carburization at 208° formed chiefly cobalt carbide, Co_2C; at 235° cobalt carbide and "free" carbon were formed; and at 275° chiefly "free" carbon. After the surface area determination or activity test, the catalyst was hydrogenated under varying conditions, and the area or activity again determined. The data of surface area and activity studies are presented in Tables VI and VII.

The surface area data (Table VI) show that the surface area of the reduced catalyst (Period 1-R) does not decrease appreciably on carburization at 208° (1-C) and on subsequent reduction at 208° (2-R); however, the volume of chemisorbed carbon monoxide decreased on carburization

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(18) V_m is the volume of physically adsorbed gas, cc. (S. T. P.), required to form a monolayer on the surface.

(19) Pores not penetrated by mercury at atmospheric pressure. See Ritter and Drake, *Ind. Eng. Chem., Anal. Ed.*, **17**, 782 (1945).

(20) In Tables III, IV and V, the space velocity of synthesis gas was constant with the temperature varied to maintain a 70% contraction. Thus the lower temperature of operation corresponds to the greater activity.

TABLE III

EFFECT OF OPERATING PRESSURE ON COBALT CATALYSTS

Tests at a space velocity per hour of 100

Test	Operating periods	Pressure, atm.	Average temp.,[a] °C.	Apparent[b] contraction, %	Products, % CH_4	$C_3 + C_4$	$C_1 - C_4$	Liquids and solids
			Pelleted[c] $Co-ThO_2$-kieselguhr catalyst 108B					
X-29	b-g	1	185 (186)	70.9	12.1	10.0	24.5	75.5
X-29	i-p	7.8	189 (186)	71.3	19.0	10.9	33.5	66.5
X-31	b-j	7.8	187	71.8	18.6	10.5	32.0	68.0
			Granular[d] $Co-ThO_2$-MgO-kieselguhr catalyst 89K					
X-17	b-k	1	186 (187)	74.4	13.1	10.2	25.6	74.4
X-17	v-z	7.8	188 (188)	72.0	14.0	8.6	23.2	76.8
			Pelleted[e] $Co-ThO_2$-MgO-kieselguhr catalyst 89J					
X-21	c-l	1	186 (186)	72.0	15.6	8.1	24.9	76.1
X-21	o-u	7.8	191 (188)	69.5	18.2	10.4	28.3	71.7

[a] The temperatures in parentheses are for the last two weeks of operation at one atmosphere and the first two weeks of operation at 7.8 atmospheres. [b] Apparent contraction computed by $100\ (1 - V_E/V_I)$ where V_E is the flow of exit gas and V_I the flow of synthesis gas. [c] Cylindrical pellets, 3.2 mm. in diameter by 3.2 mm. in length. [d] Broken filter cake. [e] Cylindrical pellets, 3.2 mm. in diameter by 1.6 mm. in length.

TABLE IV

EFFECT OF SIZE AND DENSITY OF PELLETS ON $Co-ThO_2$-KIESELGUHR CATALYST 108B AT 7.8 ATMOSPHERES

Tests at space velocity per hour of 100. Methods of reduction and induction were the same.

Test	Catalyst charge, g.	Length, mm.	Diameter, mm.	Mercury density,[a] g./cc.	Av. temp., °C.	Apparent contraction,[b] %	Products, % CH_4	$C_3 + C_4$	$C_1 - C_4$	Liquids and solids
X-45	36.8	3.17	3.2	1.13	187	71.6	19.9	11.6	34.9	65.1
X-58	44.9	6.35	3.2	1.51	191	71.4	25.8	13.4	43.4	56.6

[a] Densities determined with mercury at atmospheric pressure. [b] See note b of Table III.

TABLE V

ALTERNATE OPERATION AT 1 AND 7.8 ATMOSPHERES OF PELLETED $Co-ThO_2$-KIESELGUHR CATALYST 108B

Operating periods five to six days, space velocity = 100 per hour

Operating periods[b]	Pressure, atm.	Av. temp., °C.	Apparent contraction,[a] %	Products, % CH_4	$C_3 + C_4$	$C_1 - C_4$	Liquids and solids
e	1	187	72.1	14.9	10.8	31.9	68.0
f	1	186	70.1	15.4	16.5	34.0	66.0
g	7.8	186	67.2	21.0	13.0	34.9	65.1
h	1	191	70.3	19.2	10.0	36.4	63.6
i	7.8	188	69.9	24.6	13.4	42.5	57.5
j	1	198	69.1	..	..	..	..
k	7.8	198	71.3	41.4	10.3	53.6	46.4
l	1	207	68.7	24.6[c]	..	..	..

[a] See note b of Table III. [b] A two-hour hydrogen activation at 10° higher than the previous operating temperature preceded operating periods. [c] Approximate.

and increased on reduction to only about 50% of the chemisorption found on the freshly reduced catalyst.

Carburization at 235° (2-C) deposited carbon equivalent to 130% of carbide, and about the equivalent of carbon in Co_2C was removable by reduction at 208° (3-R). In these steps, the surface area did not change greatly, but the chemisorbed carbon monoxide was less than for the carburization 1-C and reduction 2-R. The residual carbon may be termed "free carbon" as contrasted to the readily hydrogenated carbide carbon.[6,7] Carburization at 275° (3-C) increased the carbon content to the equivalent of 418% Co_2C and increased the surface area and carbon monoxide chemisorption sizably. Reduction 4-R decreased the carbon content only slightly, and subsequent carburization at 208° (4-C) increased carbon by only the equivalent of 25% of Co_2C. Thus, after carburization at 275° the cobalt no longer contained sizable amounts of carbide, and carburization at 208° did not increase the carbide content appreciably. The surface area was increased to 50.6 square meters per gram in the carburization at 275° (3-C); the increase in area was probably that of the "free" carbon deposited in the catalyst. Hydrogenation (4-R) and carburization (4-C) at 208° did not significantly change the surface area. The volume of chemisorbed carbon monoxide after carburization at 275° was nearly equal to that after reduction 2-R.

Rereduction 5-R at 360° which was similar to 1-R removed carbon about equivalent to Co_2C, but did not increase the surface area or carbon monoxide chemisorption significantly over that of the catalyst after 3-C. Carburization 5-C at 208° increased the carbon content only by the equivalent of 30% Co_2C, indicating that carbide formation was still inhibited. In reduction 6-R at 360°, the carbon was slowly removed until after 296 hours only the equivalent of 7.9% Co_2C remained. During the rereduction, the area decreased to only slightly greater than that of the original reduced catalyst, and the volume of chemisorbed carbon monoxide increased to two-thirds of that of the original reduced catalyst. The catalyst was still poisoned with respect to formation of carbide as indicated by carburization 6-C at 208°.

A similar carburization and reduction cycle was made on $Co-ThO_2$-MgO-kieselguhr catalyst 89K. The results were very similar to the data in Table VI. After several carburization and reduction cycles at 200°, catalyst 89K was carburized at 275° until 16 times the equivalent of the carbon in Co_2C was deposited. In addition to an increase in total surface area from 62.0 sq. m. per gram for the original reduced catalyst to 149.4 sq. m. per gram the volume of chemisorbed carbon monoxide increased from 3.1 cc. (S.T.P.) per gram to 3.6 cc. (S.T.P.) per gram. (The adsorption data are given per gram of unreduced catalyst.) This indicates an increase in area of the cobalt possibly due to splitting of the metal lattice by carbon.

TABLE VI

EFFECT OF CARBURIZATION AND HYDROGENATION ON THE SURFACE AREA OF COBALT CATALYST 108B

	Treatment				Weight change on treatment, mg./g	Carbon, %, based on Co_2C	Surface area, sq. m./g.	V_m,[b] cc./g.	V_{CO},[c] cc./g.	V_{CO}/V_m
No.	SVH[a]	Gas	Temp., °C.	Hours						
	Original catalyst				.....	...	71.6	16.3	0.0	...
1-R	3000	H_2	360	2.0	−230.0	0.0	32.6	7.44	3.00	0.403
1-C	100	CO	208	15.5	+ 34.4	112.0	31.5	7.18	0.94	.131
2-R	100	H_2	208	16.0	− 34.7	6.1	30.1	6.88	1.44	.209
2-C	100	CO	235	12.5	+ 32.9	114.5	...	...	..	...
				59.5	+ 5.1	130.1	32.0	7.32	0.78	.107
3-R	100	H_2	208[d]	12.5	− 33.4	30.5	31.2	7.12	..	...
				30.7	− 0.4	29.3	31.3	7.14	0.85	.119
3-C	100	CO	275	16.0	+127.4	418.2	50.6	11.54	1.30	.113
4-R	100	H_2	208	18.0	− 7.1	398.0	50.0	11.40	1.29	.113
4-C	100	CO	208	16.0	+ 8.1	423.5	50.8	11.59	1.05	.091
5-R	3000	H_2	360	2.0	− 35.3	319.0	51.4	11.74	1.30	.111
5-C	100	CO	208	17.3	+ 10.6	354.8	52.2	11.92	..	...
6-R	3000	H_2	360	22.0	− 45.1	216.5	..	...	..	...
				64.0	− 19.8	156.1	46.8	10.7	1.48	.138
				157.3	− 20.4	93.8	..	...	..	...
				296.3[e]	− 28.1	7.8	35.2	8.03	1.99	.248
6-C	100	CO	208	18.0	+ 18.0	72.3	..	...	..	...

[a] Space velocity per hour (volumes of gas (S. T. P.) per volume catalyst per hour). [b] Volume of nitrogen necessary to form a monolayer. [c] Volume of chemisorbed carbon monoxide at −195°. [d] Temperature controller failed and temperature rose to 250° for a short period. [e] Temperature controller failed and temperature rose to 450° in part of this period.

TABLE VII

EFFECT OF CARBURIZATION AND HYDROGENATION ON ACTIVITY AND PRODUCT DISTRIBUTION OF COBALT CATALYST 108B

Space velocity of synthesis gas per hour was 100.

	Pretreatment							Products g. cu. m. of synthesis gas reacted			
Period	Gas	SVH	Temp., °C.	Hours	Hours	Av. temp., °C.	Synthesis gas reacted, %	CH_4	$C_3 + C_4$	C_1-C_4	Liquids and solids
a	H_2	3000	360	2	73	173	66.6	21.8	27.2	55.9	105.7
b	CO	100	208	16	126	195	47.4	41.8	37.8	90.1	64.4
c	H_2	100	208	16	149	190	63.8	27.7	38.7	72.6	106.9
d	CO	100	208	16	149	191	32.7	41.6	33.0	82.3	...
e	H_2	100	208	16	127	190	51.7	34.8	..	...	81.8
f	CO	100	208	16	176	193	22.9	84.3	..	...	...
g	H_2	100	208	16	126	190	42.3	...	..	...	...
h	CO	100	208	16	125	191	17.5	122.9	53.7	189.1	46.9
i	CO	100	274	15	149	191	18.9	106.3	18.5	132.3	10.6
j	H_2	100	208	16	119	191	56.3	73.5	34.5	108.2	15.8
k	H_2	100	200	2	165	189	48.9	83.2	47.2	137.4	18.4
l	H_2	3000	360	2	166	190	64.5	36.7	45.9	98.6	76.1

In Table VII are presented activity and product distribution data for another sample of catalyst 108B, tested at atmospheric pressure with two volumes of hydrogen to one volume of carbon monoxide gas. Reduction and carburization steps were arranged to be somewhat similar to those of Table VI. Before each carburization step, the catalyst was stripped of adsorbed hydrocarbons by hydrogenation for two hours at 208° to insure that the surface was accessible during the carburization. In these tests (weeks c–l) the temperature and flow of synthesis gas were held constant, and the activity was expressed as the fraction of the gas consumed, *i. e.*, the real contraction. Products are given as grams per cubic meter of synthesis gas consumed.

After carburization b at 208° the activity decreased and yields of methane and C_1–C_4 hydrocarbons were increased. Although hydrogenation at 208° (c) increased the activity and shifted the product distribution as compared with period b, the products contained a higher percentage of light hydrocarbons, and the activity was considerably lower than in operating period a. In the following carburization and reduction cycles (d to h), the hydrogenated catalyst was more active and had a more favorable product distribution than the corresponding carburized one, but the activity of the catalyst in the hydrogenated or carburized state decreased steadily, and greater fractions of methane and light hydrocarbons were formed. Thus, carbide formation has a marked effect on both activity and product distribution. Repeated cycles of carburization and reduction at 208° caused a gradual decrease in activity and a shift toward formation of lighter hydrocarbons that was super-imposed on the effect of carbide on activity and product distribution. After carburization at 275° in period i, the activity and methane formation were not significantly different from that of period h. Reduction at 208° in period j increased the activity sizably, but the product distribution was strongly shifted toward light hydrocarbons compared with period a. Reduction l at 400° increased the activity to that of period c, but distribution of products was less favorable than in the period c. Thus "free" carbon does not decrease the activity very much but has a marked effect on the product distribution.

Discussion

The Fischer–Tropsch synthesis is a slow catalytic process compared with simple reaction such as the catalytic hydrogenation of ethylene, and in no case did the synthesis proceed to equilibrium. Although the catalyst was heavily covered with wax, the rate of synthesis does not appear dependent upon diffusion: First, the temperature coefficient was considerably higher than that expected for diffusional processes,[8,10] and second, the pressure coefficient was about zero. Thus, the rate must be dependent upon the rate of some surface process that is not pressure dependent, and the linear dependency of activity on surface area should be expected.

The study of the catalyst used in the synthesis at atmospheric pressure (Tables I and II) indicated the amount of the hydrocarbon on the catalyst. Hydrogen treatment at 200° for two hours removed 90% of the adsorbed wax. Further hydrogenation at this temperature caused only a very small loss in weight. However, reduction at 400° restored the catalyst to the same condition as after the initial reduction. The surface area and pore volume were unchanged after the eleven weeks of operation. This agrees with the fact that the activity remained constant during the operation of this catalyst and the observation that the X-ray diffraction patterns of the catalyst did not change during the synthesis.[9] The results indicate that little if any "free" carbon was deposited during the synthesis. The stability of the catalyst to sintering was not entirely unexpected since the temperature of the synthesis was more than 200° lower than the reduction temperature.

Thus, the surface of catalysts operated at atmospheric pressure was heavily covered with wax, and the pores of those operated at elevated pressures were probably almost entirely filled.[5] Although catalysts operated at elevated pressure produce a greater fraction of higher molecular weight hydrocarbons, it is probable that the average molecular weight of the product in the catalyst operated at elevated pressures is lower than that in catalysts used at atmospheric pressure. At elevated pressures hydrocarbons of lower molecular weight than at atmospheric pressure should condense in the catalyst bed and should flow over the catalyst as liquid. The liquid should continuously remove higher molecular weight hydrocarbons.[14] Catalysts operated entirely at elevated pressures or at elevated pressures after several weeks of operation at atmospheric pressure had the same activity as in atmospheric pressure operation. However, activities at atmospheric pressure after operation at the higher pressure were considerably less, this effect being more pronounced when the catalyst was not hydrogen treated between periods of operation. Alternate atmospheric and pressure operation decreased the activity compared with previous periods of atmospheric and pressure operation, respectively.

In operation at atmospheric pressure, the activity remains nearly constant for two or three weeks of continuous operation followed by a rapid decrease in activity. This loss in activity may be related to the time at which the pores of the catalyst are quite completely filled with adsorbed hydrocarbon; and reactivation involves removal of this hydrocarbon by hydrogenation or solvent extraction.[5,21] The pores of the catalyst operated at elevated pressures are assumed to be quite completely filled with hydrocarbons at all times, and the activity remains constant for periods of three or more months without any reactivation. Thus, in atmospheric pressure operation it appears that pores entirely filled with hydrocarbons are considerably less accessible than only partially filled pores, but in pressure operation, the rate of diffusion of reactants is sufficient to maintain constant activity even with completely filled pores.

Parallel to the decrease in activity (Table V), the product distribution was shifted toward the formation of larger fractions of methane and other light hydrocarbons. From these and other data (Tables III and IV and refs. 10 and 12), the following generalization may be made: Decrease of the accessibility of the surface either by deposition of excessive quantities of wax by operation at elevated pressure or by decreasing the average pore diameter by pelleting causes an increase in the fraction of methane and other light hydrocarbons and in some cases a decrease in activity. In pressure operation the greater proportion of light hydrocarbons may be due to the greater rate of diffusion of hydrogen compared with that of carbon monoxide through the hydrocarbon film covering the surface as postulated by Craxford,[5] so that the gas reaching the catalyst surface is richer in hydrogen than the synthesis gas.

The conversion of the cobalt in a catalyst to carbide did not appreciably change the total surface area (1-R and 1-C of Table VI); hence, the lower activity of the carbided catalyst (b of Table VI) must be related to the presence of the carbide. The volume of chemisorbed carbon monoxide at −195° on the carbided catalyst was only one-third of that chemisorbed on the original reduced catalyst. On reduction (2-R of Table VI) the volume of chemisorbed carbon monoxide was less than half that of the original reduced sample. This may be due to poisoning by the small amount of residual carbon. Repeated carbiding and reduction at 208° decreased the activity in the corresponding reduced and carbided states compared with the original reduced and carbided states.

Accompanying the decrease in activity of carbided catalysts, the fraction of light hydrocarbons in the products increased. "Free" carbon deposited from carbon monoxide at 235° and higher temperatures had a smaller effect on activity, but the product distribution was more strongly shifted

(21) Hall and Smith, *J. Soc. Chem. Ind.*, **65**, 128 (1946).

toward light hydrocarbons than in the presence of cobalt carbide.

It was found that "free" carbon or processes accompanying its formation inhibited carbide formation from carbon monoxide at 208°, some inhibition being observed even after the "free" carbon had been decreased to 2 mg./g. of catalyst by reduction at 360° (6-R of Table VI). The data indicate that the catalytic activity was not decreased by the "free" carbon even though the extent of carbide formation was decreased. This appears to be evidence against cobalt carbide as an intermediate in the synthesis.

At least part of the greater yield of methane and light hydrocarbons from the carbided catalyst may be formed by reduction of the carbide with hydrogen of the synthesis gas, and accompanying this process the activity of the carbided catalyst increased for the first several days.[9] The higher yields of light hydrocarbons with catalysts containing "free" carbon cannot be explained in this manner since "free" carbon does not hydrogenate at synthesis temperatures. It is possible that the presence of carbon atoms decreases the extent of polymerization at the surface by breaking the continuity of cobalt atoms in the cobalt crystallites. Although deposition of large amounts of "free" carbon slightly increased the area of the cobalt surface indicating some splitting of the cobalt lattice by carbon, this increase was small compared with the increase in the total area. Thus it appears that most of the "free" carbon was deposited at the surface and not within the crystallites of cobalt.

The results presented in this paper are in general agreement with those of Craxford.[3,4,5] The present paper and a previous one[9] show that the presence of bulk phase carbide decreased the catalytic activity and that bulk phase carbide was not formed in the synthesis. Thus, carbide if present at all in the catalyst in the synthesis must reside near the surface. In a recent paper[5] Craxford has postulated a surface carbide as an intermediate in the synthesis, because in his catalysts the cobalt atoms must be distributed into layers less than two atoms thick to account for the observed surface area. For purposes of reaction mechanisms the distinction between surface carbide and chemisorbed carbon monoxide is difficult.

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Summary

1. The surface of a catalyst used in the synthesis was found to be heavily covered with hydrocarbon. Hydrogenation at 200° removed 90% of these adsorbed hydrocarbons, and reduction with hydrogen at 400° restored the catalyst to the same condition as after the initial reduction. There was no evidence of sintering of the catalyst or of carbon deposition.

2. Activity data for operation at 1 and 7.8 atmospheres are related to the adsorbed hydrocarbon film.

3. Decrease in the accessibility of the surface of these catalysts either by deposition of excessive quantities of wax or by reduction of average pore diameter by pelleting caused an increase in the fraction of methane and other light hydrocarbons and in some cases a decrease in activity.

4. The presence of bulk phase carbide in these catalysts caused a marked decrease in activity, but "free" carbon did not affect the activity very much. The presence of carbon in both forms shifted the product distribution toward light hydrocarbons. The surface area did not change appreciably when the cobalt in the catalysts was converted to cobalt carbide. Carburization at 275°, under conditions which form predominantly "free" carbon, increased the area sizably.

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