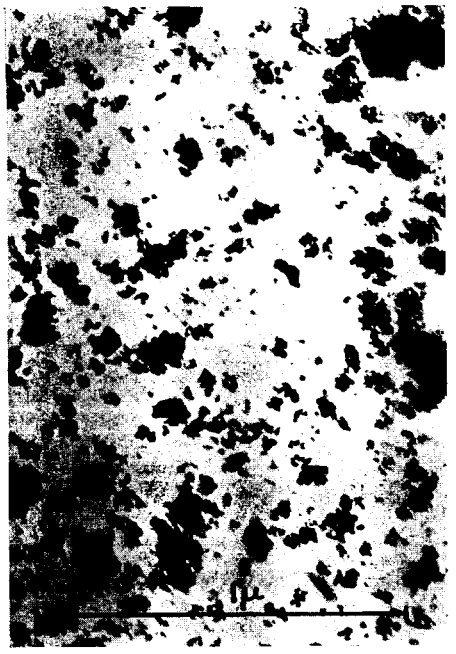
12

13

14



15

FIGURE 4.—Electron Micrographs of Cobalt Basic Carbonate and Cobalt Basic Carbonate Plus Promoters:

12, Cobalt basic carbonate; *13*, same, reduced at 250° C.; *14*, same, reduced at 400° C.; *15*, reduced basic carbonate plus thoria and magnesia.

as the metal shrinks about the particles of kieselguhr. A sizable fraction of the decrease in surface area observed in these studies probably occurred during reduction and was not caused by sintering of the unreduced material. Immediately after removal of oxygen the metal atoms may be in a very unstable state, and considerable reorientation and sintering may result from (1) the tendency to form relatively stable crystallites or aggregates of metal atoms and (2) the decrease in surface energy by diminution of surface area. Pro-

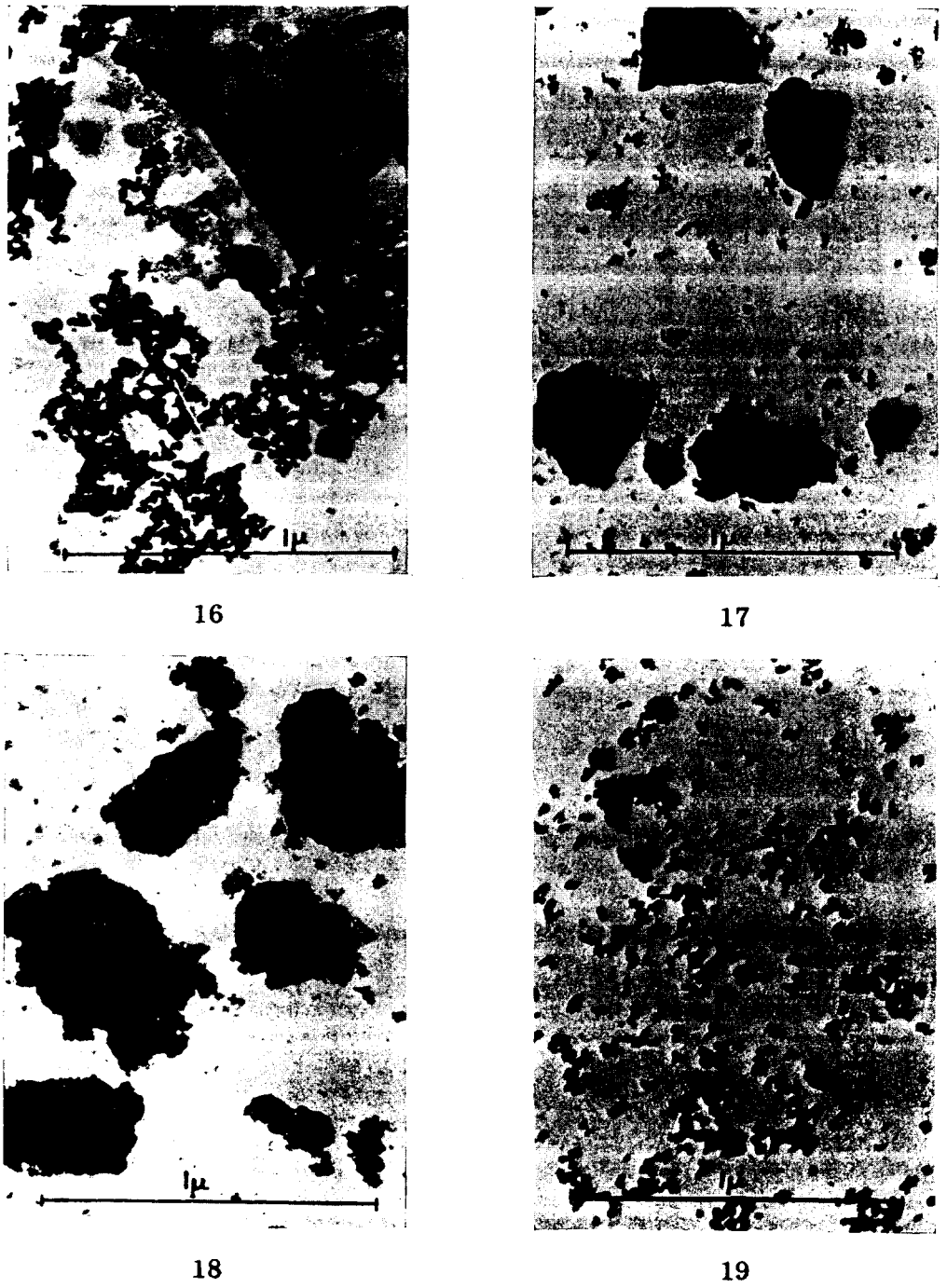


FIGURE 5.—Electron Micrographs of Precipitated Cobalt and Iron Catalysts:

16, Reduced-cobalt basic carbonate plus kieselguhr: *17*, reduced cobalt-thoria-magnesia-kieselguhr catalyst: *18*, ferric oxide-copper oxide-potassium carbonate catalyst; *19*, same, treated with $1H_2 + 1CO$ gas at 230° C.

TABLE 6.—*Comparison of particle diameter and surface areas from electron micrographs and nitrogen-adsorption measurements*

Micrograph No.	Preparation	Surface area,[1] m.²/gm.	Weight loss, percent	Density, gm./cc.	Average particle diameter, $\bar{d}$, microns [2]		Surface areas, m.²/gm.[3]	
					From electron micrographs	From nitrogen adsorption	From electron micrographs	From nitrogen adsorption
1	Hydrous ferric oxide gel	178. 5		3. 4–3. 9	0. 51	0. 0093	3. 2	178. 5
2	Hydrous ferric oxide gel, reduced	1. 8	27. 1	7. 9	. 17	[4] . 31	4. 5	[4] 2. 5
4	Nickel oxide	153. 0		4. 4	2. 2	. 0089	. 6	153. 0
5	Nickel oxide, reduced	3. 6	39. 6	8. 9	. 57	. 11	1. 2	6. 0
6	Copper oxide	65. 4		6. 4	. 037	. 014	25. 3	65. 4
7	Copper oxide, reduced	5. 5	20. 8	8. 9	. 13	. 10	5. 2	6. 9
8	Silver oxide	1. 7		7. 1	. 62	. 49	1. 4	1. 7
9	Silver oxide, reduced	. 3	7. 5	10. 5	. 59	1. 7	1. 0	. 3
10	Cobaltous oxide	67. 0		5. 7	. 27	. 016	3. 9	67. 0
11	Cobaltous oxide, reduced	3. 2	30. 2	8. 9	. 38	. 15	1. 8	4. 6
12	Cobalt basic carbonate	126. 2		3. 8	. 010	. 013	157. 9	126. 2
14	Cobalt basic carbonate, reduced at 400° C.	2. 5	44. 2	8. 9	. 22	. 150	3. 1	4. 5
15	Cobalt-thoria-magnesia, reduced	52. 8	37. 7	7. 8	. 011	. 0091	69. 9	84. 8
16	Cobalt-kieselguhr, reduced	14. 2	21. 1	[5] 8. 9	. 028	. 027	24. 1	25. 6
17	Cobalt-thoria-magnesia-kieselguhr, reduced	133. 2	16. 7	[5] 7. 8	. 010	. 0038	76. 9	204. 9
18	Ferric oxide catalyst	303. 0		5. 3	1. 3	. 0037	. 90	303. 0
19	Ferric oxide catalyst, reduced	22. 9	10. 3	6. 0	. 024	. 039	41. 7	25. 5

[1] Surface area per gram of unreduced catalyst.

[2] Average diameter defined by $\bar{d}\ \Sigma d^3/\Sigma d^2$; these average diameters are estimated from the ratio of pore volume to surface area. For catalysts containing kieselguhr, the average diameter is given for the cobalt-promoter complex.

[3] Surface areas per gram of unreduced or reduced material. For catalysts containing kieselguhr, the area is given for cobalt-promoter complex per gram of unreduced or reduced catalyst.

[4] The adsorption measurement was made on a different sample of the same ferric oxide that was reduced in hydrogen for 60 hours at 415° C. This is very probably the reason why the area from nitrogen adsorption is less than that estimated from the electron micrographs.

[5] Density of the cobalt-promoter complex.

moters and carriers should inhibit these processes.

CARBURIZED CATALYSTS

The surface characteristics of pelleted cobalt-thoria-kieselguhr catalyst 108B carburized in carbon monoxide at atmospheric pressure and 208°, 235°, and 275° C. were studied.[34] After determination of the surface area the catalyst was hydrogenated under varying conditions. After each step of hydrogenation or carburization the adsorption of nitrogen and then carbon monoxide, both at −195° C., was determined as shown in table 7. The surface area of the reduced catalyst (period 1–R) did not change appreciably on carburization at 208° C. (1–C) or on subsequent reduction at 208° C. (2–R); however, the volume of chemisorbed carbon monoxide decreased on carburization and increased on rereduction to only about 50 percent of that found on the freshly reduced catalyst.

After carburization at 275° C. the cobalt catalyst did not contain sizable amounts of carbidic carbon, and further carburization at 208° C. (4–C) did not increase the carbide content appreciably. Rereduction (5–R) at 360° C. removed an amount of carbon about equivalent to Co_2C but did not increase the capacity for chemisorption of carbon monoxide significantly over that of the carburized catalyst (after 3–C). Carburization (5–C) at 208° C. increased the carbon content only to the equivalent of 30 percent of Co_2C, indicating that carbide formation was still inhibited. In rereduction (6–R) at 360° C. the carbon was slowly removed until, after 296 hours, the equivalent of only 7.9 percent of Co_2C remained. During the rereduction, the area decreased so that it was only slightly greater than that of the original reduced catalyst, but the volume of chemisorbed carbon monoxide after rereduction was two-thirds that of the original reduced catalyst. Formation of carbide was still inhibited, as indicated by recarburization (6–C) at 208° C. Similar results were obtained with cobalt-thoria-magnesia-kieselguhr catalyst 89J (see also table 7).

Thus, deposition of carbidic carbon does not affect the surface area, but deposition of free carbon greatly increases it. Both forms of

[34] Anderson, R. B., Hall, W. K., Krieg, A., and Seligman, B., Studies of the Fischer-Tropsch Synthesis. V. Activities and Surface Areas of Reduced and Carburized Cobalt Catalysts: Jour. Am. Chem. Soc., vol. 71, 1949, pp. 183–188.

TABLE 7.—*Effect of carburization and hydrogenation on the surface area of cobalt catalysts 108B and 89J*

[All data per gram of unreduced catalyst]

No.	Treatment				Weight change on treatment, mg./gm.	Carbide based on Co_2C, percent	Surface area, $m.^2$/gm.	V_m, cc./gm.[2]	V_{CO}, cc./gm.[3]	$\frac{V_{CO}}{V_m}$
	S. V. H.[1]	Gas	Temp., ° C.	Time, hours						
Catalyst 108B										
Original catalyst							71.6	16.3	0.0	
1-R	3,000	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	.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	.78	.107
3-R	100	H_2	[4] 208	12.5	−33.4	30.5	31.2	7.12		
				30.7	−.4	29.3	31.3	7.14	.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	3,000	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	3,000	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				
				[5] 296.3	−28.1	7.8	35.2	8.03	1.99	.248
6-C	100	CO	208	18.0	+18.0	72.3				
Catalyst 89J										
Original catalyst							90.2	20.6	0.0	
1-R		H_2	400	2.5	−177.5	0.0	62.0	14.2	3.1	0.218
1-C		CO	200	16.0	+24.4	107.5	52.4	12.0	1.3	.108
2-R		H_2	203	7.0	−18.6	26.9	58.4	13.8	2.5	.181
			265	8.0						
3-R		H_2	250	19.5	−1.0	20.7				
3-C		CO	200	16.0	+23.0	125.1	52.4	12.0		
4-R		H_2	275	16.0		44.0	53.4	12.2	1.6	.131
4-C		CO	275	5.0	+87.6	426	74.1	16.9	1.3	.077
5-R		H_2	275	16.0	−14.5	366	75.2	17.2	1.9	.111
5-C		CO	275	16.0	+260.1	1,613	149.4	34.1	3.6	.105

[1] Space velocity per hour=volumes of gas (STP) per volume catalyst per hour.
[2] Volume of nitrogen necessary to form a monolayer.
[3] Volume of chemisorbed carbon monoxide at −195°C.
[4] Temperature controller failed, and temperature rose to 250°C. for a short period.
[5] Temperature controller failed, and temperature rose to 450°C. in part of this period.

carbon decrease the capacity of the catalyst for chemisorption of carbon monoxide at −195° C., and elemental carbon inhibits the formation of carbide at 208° C.

USED CATALYSTS

After 12 weeks' operation in the synthesis at 183°C. with $2H_2+1CO$ gas at atmospheric pressure, pelleted catalyst 89FF (cobalt-thoria-magnesia-kieselguhr) was removed from the reactor for studies of surface properties.[35] Each week of operation included 5 days of synthesis (except for 4 days in the 12th week), followed by reactivation with hydrogen for 2 hours at 195° C. and for 44 hours at 150° C. in a slow stream of hydrogen. As indicated in table 8, about 90 percent of the adsorbed hydrocarbons on the used catalyst was removed by hydrogenation at 200° C. for 2 hours; further hydrogen treatment at this temperature resulted in only a very small loss in weight. Thus, most of the removed hydrocarbons must have been formed in the last 4 days of synthesis. The adsorption data and mercury and helium densities show that the catalyst surface is heavily covered with hydrocarbons in its normal operating condition at atmospheric pressure. In pressure operation the pores of the catalyst are believed to be completely filled with hydrocarbon product at all times.[36] Reduction at 400° C., however, restored the catalyst to the same condition as after the initial reduction. Surface area, pore volume, activity, and structure of the catalyst remained unchanged after 11 weeks of operation. Thus, no appreciable structural changes occurred in the catalyst during synthesis, and little or no free carbon was deposited.

X-ray diffraction patterns of a large number of cobalt-type catalysts that had been used in the synthesis show (table 9) that all the samples except the completely amorphous German catalysts contained disordered cobalt with the same diffraction pattern as a freshly reduced catalyst. These results indicate that no appreciable fraction of the cobalt had passed through a carburization-hydrogenation cycle during the synthesis, as conversion to carbide and subse-

[35] Work cited in footnote 34, p. 15.

[36] Craxford, S. R., The Chemistry of the Fischer-Tropsch Synthesis: Fuel, vol. 26, 1947, pp. 119-123.

TABLE 8.—*Adsorption, density, and pore volume data for reduced and used cobalt catalyst 89FF*

Adsorption data per gram of unreduced catalyst

Treatment	Cumulative weight loss, percent [1]	Surface area, m.²/gm.	V_m [2] cc./gm.	V_{CO} [3] cc./gm.	$\frac{V_{CO}}{V_m}$	d_{He}, cc./gm.	d_{Hg}, cc./gm.	Pore volume, cc./gm.
a. Reduced 2 hr. with H_2 at 400° C.; SVH=6,000 [4]		80. 8	18. 45	3. 2	0. 173	3. 031	1. 138	[5] 0. 549
b. Used (*a*) plus 12 weeks of synthesis	0. 0	4. 36	1. 00	. 13	. 130	1. 891	1. 471	[6] . 201
c. (*b*) plus 2 hr. with H_2 at 200° C.; SVH=200	23. 5	70. 5	16. 1	2. 7	. 168	2. 881		[5] . 151
d. (*c*) plus 20 hr. with H_2 at 200°C.; SVH=200	23. 7	74. 2	16. 9	3. 2	. 189	3. 007	1. 112	[5] . 566
e. (*d*) plus 2 hr. with H_2 at 400° C.; SVH=6,000	25. 3	79. 1	18. 1	3. 8	. 210			

[1] Weight based on weight of used catalyst as removed from converter.
[2] Volume of nitrogen corresponding to a physically adsorbed monolayer.
[3] Volume of carbon monoxide chemisorbed at −195° C.
[4] Space velocity per hour, volumes of gas (STP) per volume of catalyst per hour.
[5] Pore volume in cubic centimeters per gram of reduced catalyst.
[6] Pore volume in cubic centimeters per gram of catalyst as removed from converter.

TABLE 9.—*Debye-Scherrer X-ray patterns of used cobalt catalysts*

Test No., X-	Type of kieselguhr	Synthesis operation: Weeks	Synthesis operation: Temp., ° C.	Synthesis operation: Pressure, atm.	X-ray diffraction analysis: Phases detected	X-ray diffraction analysis: Diffuseness [1]
89 type—100Co : 6ThO_2 : 12MgO : 200 kieselguhr						
17	Natural	15	185	1	Disordered cobalt	C
			185	7.8		
19	do	35	177	1	do	X
23	F. cal	34	192	1	Crystobalite, disordered cobalt.	B
24	do	11	194	1	do	B
26	Natural	15	192	1	do	X
28	F. cal	9	193	1	do	B
35	Natural	14	190	1	Disordered cobalt	B
41	do	10	185	1	do	B
48	do	12	179	1	do	B
53	Calcined	12	185	1	Quartz	B
57	Natural	9	188	1	Disordered cobalt	X
108-type—100Co : 18ThO_2 : 100 kieselguhr						
29	Natural	7	184	1	Disordered cobalt	B
		9	189	7.8	do	B
31	do	10	186	7.8	do	B
37	do	12	186	7.8	do	B
40	do	1	178	7.8	do	B
43	do	10	187	7.8	do	B
45	do	12	187	7.8	do	B
46	do	13	188	1	do	B
50	do	12	186	7.8	do	B
68	do	7	185	7.8	do	C

[1] B=diffuse; C=very diffuse; X=diffuse, difficult to interpret.

quent hydrogenation at synthesis temperatures converts disordered cobalt to the h. c. p. phase.

REDUCTION OF COBALT CATALYSTS

The results of studies by Ruhrchemie[37 38] showed that the reducibility of a cobalt catalyst was affected by a number of conditions. For cobalt-thoria-kieselguhr and cobalt-thoria-magnesia-kieselguhr catalysts the ease of reduction decreased as the kieselguhr content was increased from 100 to 1,000 parts per 100 parts of cobalt. For cobalt-magnesia-kieselguhr catalyst, however, no change in ease of reduction was observed over this range of kieselguhr content. A comparison of catalysts that contained 100Co : 100 kieselguhr and that were reduced at the same temperature showed that the reducibility varied also with the type of promoter, the rate of reduction being greater with thoria than with thoria-magnesia. In addition, reduction was facilitated by the presence of such impurities as nickel and copper.

By varying the reduction temperature and maintaining other conditions fixed, a catalyst containing 100Co : 5ThO_2 : 10MgO : 200 kieselguhr was reduced 15 percent at 300° C., 45 percent at 325° C., and 75 percent at 350° C. in the same time interval (time of reduction not given).[39] A catalyst containing magnesia as a promoter precipitated on magnesia as a carrier (100Co : 15MgO : 75MgO) was only 24 percent reduced at 450° C. Roelen [40] found that the presence of carbon dioxide and/or water vapor in the reducing gas hinders the reduction of cobalt catalysts. Reduction in the presence of 1 percent of water vapor yielded only 50 percent of metallic cobalt, while reduction under the same conditions, but with a dry gas mixture, yielded 81 percent of metal, and the extent of reduction decreased as the percentage of water vapor increased.[41] Analysis of the exit gases indicated that carbon dioxide was released from

[37] Hall, C. C., and Craxford, S. R., Additional Information Concerning the Fischer-Tropsch Process and Its Products: BIOS Final Rept. 1722, 1946, 178 pp.; PB 93,498.
[38] Schenk, P., Reducibility of Cobalt Catalysts: FIAT Reel K29, frames 7,134–7,135, May 12, 1938; PB 70,218, TOM Reel 296.
[39] Work cited in footnote 37 above.
[40] Hall, C. C., Craxford, S. R., and Gall, D., Interrogation of Dr. Otto Roelen of Ruhrchemie A. G.: BIOS Final Rept. 447, 1945, 59 pp.; PB 77,705; TOM reel 226.
[41] Roelen, O., Reduction With Hydrogen Containing a Foreign Gas: TOM reel 288, frames 792–805, April 1937.

the basic carbonate of the catalyst and that methane was produced. With hydrogen containing 3 percent of carbon dioxide, only 11.5 percent of cobalt metal was produced, even after a threefold increase in time. Analysis of the exit gases showed that the concentration of carbon dioxide decreased and that of methane increased, probably according to the reaction

$$CO_2+4H_2\rightarrow CH_4+2H_2O. \quad (1)$$

The effect of reduction conditions on the extent of reduction was not studied by the Bureau of Mines. The influence of small modifications of reduction and induction procedures on synthesis behavior was investigated, as shown in table 10. In general, these modifications had no significant effect on activity (as indicated by average temperature required for a conversion of about 70 percent) or selectivity. These data also show that the synthesis rate is independent of operating pressure in the range 1 to 7.8 atmospheres.

KIESELGUHR IN COBALT CATALYSTS

PROPERTIES

Little published information is available to indicate the suitability of a given kieselguhr as a catalyst carrier. Some properties and uses of kieselguhrs and microscopic studies have been reported by Calvert,[42] Ries,[43] and Turkevich.[44] More pertinent is a report of German kieselguhr studies in documents captured by the Technical Oil Mission teams at the end of World War II.[45] Bureau of Mines studies on the properties of kieselguhrs include X-ray diffraction and chemical analyses, electron microscope studies, and surface area, density, and pore-volume determinations.[46] [47]

Additional data [48] obtained for more than a dozen kieselguhrs are summarized in tables 11 and 12. Table 11 shows that the untreated kieselguhrs were chiefly amorphous to X-ray diffraction, whereas the calcined and flux-calcined preparations produced patterns of quartz and/or cristobalite. Slight differences among these kieselguhrs occurred with respect to the quantity of crystalline matter; for

[42] Calvert, R., Diatomaceous Earth: Chemical Catalog Co., New York, N. Y., 1930.
[43] Ries, H. E., Jr., Van Nostrand, R. A., and Teter, J. W., Surface Area of Catalysts. Effect of Sintering on Area and Structure of a Supported Catalyst and Its Components: Ind. Eng. Chem., vol. 37, 1945, pp. 310–317.
[44] Turkevich, J., Electron Microscopy of Catalysts: Jour. Chem. Phys., vol. 13, 1945, pp. 235–239.
[45] Work cited in footnote 8, p. 3.
[46] Work cited in footnote 5, p. 3.
[47] Skinner, K. G., Dammann, A. A., Swift, R. E., Eyerly, G. B., and Shuck, G. R., Jr., Diatomites of the Pacific Northwest as Filter Aids: Bureau of Mines Bull. 460, 1944, 87 pp.
[48] Anderson, R. B., McCartney, J. T., Hall, W. K., and Hofer, L. J. E., Kieselguhrs. Suitability as Carriers in Catalysts: Ind. Eng. Chem., vol. 39, 1947, pp. 1618–1628.

TABLE 10.—*Reduction and induction studies of cobalt catalysts*

Space velocity of $2H_2$: 1CO gas=100 hr.$^{-1}$, except where noted

Reduction [1]	Induction		Weight of catalyst, gm.	Duration of test, hr.	Synthesis		Hydrocarbon products C_5+, wt.-percent of total
	Procedure [2]	Pressure, atm.			Pressure, atm.	Temp., ° C.	
Catalyst 108B (100Co : 18ThO_2 : 100 kieselguhr); pellets 3.2 mm. long × 3.2-mm. diameter							
A	G	1	38.8	658	1	185	75.4
A	G	1	38.8	891	7	189	66.5
A	F	7	36.0	1,000	7	187	68.0
B	G	1	38.0	571	1	187	69.8
D	F	7	36.5	1,127	7	187	62.6
D [3]	G	7	36.5	801	7	[4] 191	59.4
D	G	7	37.5	1,094	7	186	63.8
C	G	7	36.8	1,143	7	187	63.8
D	G	1	37.6	1,141	1	181	74.2
Catalyst 89K (100Co : 6ThO_2 : 12MgO : 200 kieselguhr); granules, 6- to 10-mesh							
E	G	1	16.9	1,045	1	186	73.9
E	F	1	16.0	1,040	1	188	74.8

[1] Reduction procedures: *A*, Temperature raised from 250° to 360° C. in 8 hours and maintained for 2 hours at 360° C. in hydrogen at an hourly space velocity of 250; *B*, 4 hours at 360° C. in hydrogen at an hourly space velocity of 500; *C*, 4 hours at 360° C. with an hourly space velocity of hydrogen of 1,000; *D*, 2 hours at 360° C. with an hourly space velocity of 3,000; *E*, 2 hours at 400° C. with hydrogen at an hourly space velocity of 3,000. All reductions were made at atmospheric pressure.

[2] Induction procedures: *F*, Contraction schedule: Within 30 min. after synthesis gas was introduced at 150° C. the temperature was increased until a contraction of 45–50 percent was obtained, 175° C. being the upper limit. After 48 hours the temperature was increased to maintain the same contraction, 180° C. being the upper limit, and after 24 additional hours the temperature was increased to produce a contraction of 70–75 percent. *G*, Temperature schedule: Synthesis gas was introduced at 150° C. and temperature increased to 175° C. within 1 hour. After 48 hours temperature was increased to 180° C. and after 24 additional hours to temperature necessary to maintain 70–75 percent contraction.

[3] Space velocity of synthesis gas=120 hr.$^{-1}$

[4] Temperature high because of higher space velocity.

TABLE 11.—*X-ray diffraction data on kieselguhrs*

Name	Description	Diffuseness	Phase
J. M. Hyflo Super-Cel	Flux-calcined, marine; Lompoc, Calif	A	Cristobalite.
J. M. I [1]	do	A	Do.
Dicalite speed flow [2]	Flux-calcined, probably marine; Lompoc, Calif	B	Cristobalite, quartz.
Dicalite P. S [2]	do	C−	Cristobalite.
J. M. II [1]	Calcined, marine; Lompoc, Calif	C	Do.
Portuguese	Probably heated, fresh-water; Portugal	C−	Amorphous, quartz.
German	Probably heated; probably Röstguhr	C	Quartz.
J. M. III [1]	Untreated, marine; Lompoc, Calif	X	Amorphous.
J. M. IV [1]	do	X	Do.
J. M. Filter-Cel	do	C−	Amorphous, quartz, unknown.
J. M. Filter-Cel-A [3]		C−	Amorphous, quartz.
Dicalite 637T	Untreated, fresh-water; Nevada	X	Amorphous.
Dicalite 658T	Untreated, fresh-water; Washington	X	Do.
Dicalite SA5	Untreated, fresh-water; Nevada	X	Do.
Dicalite 911	Untreated, fresh-water; Terrebonne, Oreg	X	Do.
Dicalite, grade 1	do	X	Do.
Shasta County	Untreated, fresh-water; Shasta County, Calif	C−	Amorphous, unknown.

A, Sharp; B, somewhat diffuse; C, diffuse; C—, diffuse to the point where phases are difficult to discern; X, amorphous.

[1] Catalyst support. [2] Filter aid. [3] Acid-extracted.

example, a number of faint lines occurred in the Filter-Cel patterns, some of which disappeared on acid extraction. The lines that remained seem to be those of quartz. The pattern of the Portuguese kieselguhr, as far as the faint lines were concerned, was very similar to the acid-extracted Filter-Cel. The pattern of the Shasta County kieselguhr contained faint lines that cannot be assigned to quartz or any other crystalline silica. The large amount of impurities—8.0 percent as compared with 2.9 percent for Filter-Cel and 1.4 percent for acid-extracted Filter-Cel—suggests that the strange lines were due to crystalline impurities. The other amorphous kieselguhrs gave very few faint lines. The X-ray diffraction analysis of the heat-treated kieselguhrs was much more satisfactory, since the diffraction patterns were much sharper in every instance.

Silica exists in at least seven crystalline forms,

TABLE 12.—*Surface areas and pore volumes of kieselguhrs*

Name	Surface area, m.²/gm.	Bulk density cc./gm.	Hg density, cc./gm.	He density, cc./gm.	Void space,[1] cc./gm.	Pore volume,[1] cc./gm.	Average pore diameter,[2] microns
J. M. Hyflo-Super-Cel	1. 9	0. 22	0. 361	2. 27	1. 77	2. 33	4. 9
J. M. I	3. 2	. 26	. 381	2. 43	1. 22	2. 21	2. 8
Dicalite Speedflow	3. 5	. 214	. 372	2. 34	1. 94	2. 26	2. 6
Dicalite PS	3. 2	. 245	. 372	[3]	1. 39	2. 26	3. 0
J. M. II	5. 5	. 20	. 346	2. 24	2. 12	2. 46	1. 8
Portuguese	17. 5	. 345	. 508	2. 36	. 90	1. 54	. 40
German	14. 9	. 137	. 272	2. 29	3. 63	3. 24	. 87
J. M. III	19. 2	. 174	. 323	2. 35	2. 64	2. 67	. 56
J. M. IV	12. 4	. 228	. 406	2. 22	1. 92	2. 01	. 66
J. M. Filter-Cel [4]	22. 8	. 149	. 299	2. 19	3. 32	2. 81	. 51
J. M. Filter-Cel-A	20. 8	. 17					
J. M. Snow Floss [5]	19. 4	. 186	. 343	2. 33	2. 46	2. 48	. 52
Dicalite 637T	34. 2	. 196	. 369	[3]	2. 39	2. 28	. 28
Dicalite 658T	25. 4	. 215	. 335	2. 20	1. 67	2. 55	. 40
Dicalite SA5	37. 7	. 203	. 372	2. 05	2. 23	2. 20	. 24
Dicalite 911	29. 7	. 245	. 373	2. 25	1. 41	2. 29	. 31
Dicalite, Grade 1	20. 3	. 179	. 348	2. 35	2. 71	2. 44	. 49
Shasta County	33. 6	. 35	. 425	2. 39	. 51	1. 92	. 23

[1] Void space is volume of pores with openings larger than 5 microns in diameter (pores filled by mercury at atmospheric pressure) and is defined as the difference of the reciprocals of the bulk and mercury densities. Pore volume is volume of pores with openings smaller than 5 microns (pores not filled by mercury at atmospheric pressure) and is defined as the difference of the reciprocals of the mercury and helium densities.

[2] Average pore diameter computed by $d=\frac{4\times\text{pore volume}}{\text{surface area}}$.

[3] Not determined. Assumed to be 2.3 for pore-volume estimation.

[4] Acid-extracted.

[5] Untreated marine kieselguhr from Lompoc, Calif., characterized by a very small particle size, filter aid.

which may be classified into a quartz, a tridymite, and a cristobalite series. Transitions from one series to another are sluggish, whereas within each series transitions are in general very rapid. At room temperature only one member of each series usually exists: α-quartz, α-tridymite, and α-cristobalite. The last two owe their existence to the slowness of the transition from one series to another. The only forms of silica that have an accessible region of thermodynamic stability are α-quartz, β-quartz, γ-tridymite, and β-cristobalite. The various forms and their relations are shown in figure 6.

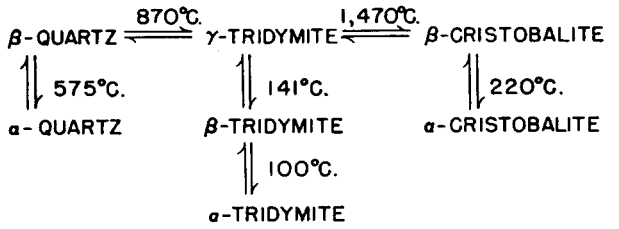


FIGURE 6.—Transitions of Silica.

Johns-Manville Type I, Johns-Manville Type II, Hyflo Super-Cel, Dicalite Speedflow, and Dicalite PS filler all contained cristobalite. In addition, Dicalite Speedflow contained α-quartz, indicating incomplete conversion from quartz to cristobalite. Normally one might expect direct transition from the low-temperature stable form (quartz) to the form stable above the transition point (tridymite). Probably none of the calcined kieselguhrs was heated above 1,470° C., where cristobalite is stable, since this would require exceedingly expensive equipment.

The cause of the formation of cristobalite in a temperature range where it is known to be metastable lies in the kinetics of the transition. Between 870° and 1,470° C.—the stability region of tridymite—quartz changes to cristobalite much more rapidly than to tridymite, and cristobalite itself changes to tridymite very slowly.

The sharpness of the lines of German kieselguhr probably resulted from heat treatment; but the absence of cristobalite suggests that the transition temperature—870° C.—probably had not been exceeded during this calcination.

Surface areas and pore volumes for the various kieselguhrs are assembled in table 12. These data are significant for catalysis, as the pore structure and density of catalysts depend, at least to some extent, on these properties. The surface areas varied from 15 to 37 square meters per gram for the untreated kieselguhrs and from 2 to 6 square meters per gram for the calcined and flux-calcined samples. Calcined and flux-calcined kieselguhrs showed less fine structure than the untreated samples. Calcination probably destroyed much of the fine structure and coalesced some pores with adjacent ones so that small pores disappeared. This result is reflected in the large pore diameters of calcined and flux-calcined kieselguhrs as compared with those of untreated kieselguhrs.

FUNCTION

The effect of the type of kieselguhr on the activity of catalysts has already been indicated.[49] Catalysts prepared with flux-calcined kieselguhr were less active than those containing untreated kieselguhrs. Cobalt catalysts prepared with calcined kieselguhr were considerably more active than those containing flux-calcined kieselguhr, but less active than those supported on untreated kieselguhr. The activities of catalysts containing untreated kieselguhrs of marine and fresh-water origin were similar. In order to make a reliable comparison of these various tests, values were computed expressing activity as cubic centimeters (STP) of $2H_2$:1CO gas converted per gram of unreduced catalyst per hour at 185° C. Table 13 shows these results and confirms the above conclusions on the relative merits of the flux-calcined, calcined, and untreated kieselguhrs.[50]

Of catalysts containing untreated kieselguhrs, the more active contained smaller amounts of acid-extractable iron (table 13). The kieselguhrs had been heated in 8N nitric acid for 2 hours to remove any impurities that would have been dissolved and reprecipitated during catalyst preparation, and the resulting solutions were analyzed for aluminum, iron, calcium, phosphate, and sulfate. Only very small amounts of impurities were removable from these calcined kieselguhrs. The low activity of catalysts containing these kieselguhrs probably can be attributed to the low surface areas of the catalysts or to the orderly crystal structure of the kieselguhr.

From the above results it would appear desirable to use an acid-extracted, unheated kieselguhr in preparing precipitated cobalt catalysts. No correlation was found for the uncalcined kieselguhrs between catalyst activity and surface area, particle size, or external or internal structure of the support. For example, the activities of catalysts prepared from untreated kieselguhrs of very small particle size (Snow Floss and Portuguese) were 86.6 and 166.3 cc. per gram per hour, respectively; this was the maximum difference observed in the tests with catalysts containing untreated kieselguhrs. The effect of differences in surface area, particle size, and structure may have been obscured by the influence of impurities and by

[49] Work cited in footnote 5, p. 3.

[50] Anderson, R. B., Krieg, A., Seligman, B., and Tarn, W., Studies of the Fischer-Tropsch Synthesis. III. Influence of Type of Kieselguhrs on Cobalt Catalysts: Ind. Eng. Chem., vol. 40, 1948, pp. 2347-2350.

TABLE 13.—*Effect of kieselguhr on activity of cobalt-thoria-magnesia-kieselguhr catalysts*

Kieselguhr	Catalyst	Test	Duration of test, hours	Activity,[1] c. c./gm. per hr.	Surface area of kieselguhr, m.²/gm.	Weight-percent extractable [2]				
						Al^{+3}	Fe^{+3}	Ca^{+2}	PO_4^{-3}	SO_4^{-2}
Flux-calcined:										
HSC	89I	X-23	1, 059	63	1. 9	0. 05	0. 03	0. 00	0. 00	0. 00
HSC	89L	X-14	1, 201	52	1. 9					
HSC	89H	X-24	1, 063	49	1. 9					
HSC	89N [3]	X-20	508	45	1. 9					
Calcined: J. M. II	89BB	X-53	1, 071	88	5. 5	. 17	. 04	. 00	. 13	. 09
Untreated, marine:										
J. M. F. C	89J	X-21	1, 075	127	22. 2	1. 23	. 75	. 12	. 09	. 11
J. M. F. C	89J	X-41	1, 030	124	22. 2					
J. M. F. C.-A [4]	89O	X-22	1, 060	167	20. 8	. 00	. 00	. 00	. 00	. 00
J. M. F. C.-A [5]	89FF	X-92	1, 030	115	24. 1	. 00	. 00	. 00	. 00	. 00
S. M. Snow Floss	89DD	X-70	1, 030	87	19. 1	. 80	. 70	. 28	. 15	. 12
Untreated, fresh-water:										
Dicalite 911	89V	X-38	1, 150	93	29. 3	1. 41	1. 14	. 35	. 00	. 26
Dicalite 911-A	89GG	X-93	1, 155	164	39. 2	. 00	. 00	. 00	. 00	. 00
Dicalite SA5	89Y	X-48	1, 145	111	37. 3					
Dicalite 658T	89Z	X-49	1, 120	95	25. 2	. 76	1. 77	. 14	. 00	. 23
Portuguese	89K	X-19	1, 070	166	17. 5	1. 61	. 65	. 00	. 00	. 11
Portuguese	89Q	X-27	1, 100	120	17. 5					
German	89U	X-35	1, 150	80	14. 9	. 43	1. 49	. 02	. 00	. 56

[1] Computed activity at 185° C., expressed as cubic centimeters (STP) of $2H_2$:1CO gas converted per gram of unreduced catalyst per hour.
[2] By heating in 8N nitric acid for 2 hours.
[3] Alkali-washed magnesia.
[4] Kieselguhr was extracted with hot nitric acid for 6 hours, washed, dried, and heated at 650° C. for 2 hours. The extraction decreased the percentages of aluminum and iron by about 50 percent.
[5] Kieselguhr was extracted with hydrochloric-nitric acid solution (1 volume each of concentrated acid and 2 volumes of water) for 16 hours at room temperature. Then it was washed and dried at 400° C.

the variability in activity of different batches of catalyst.

Kieselguhr as a carrier in cobalt Fischer-Tropsch catalysts functions to establish and maintain structures of high surface area and high porosity during preparation, pretreatment, and synthesis. The kieselguhr provides a framework (like a microscopic brushpile) that defines the bulk volume of the catalyst. This brushpile structure maintains a constant bulk volume of particles during reduction, whereas the bulk volumes of unsupported preparations decrease by factors of 2 to 8. In addition, catalysts containing kieselguhr have higher surface areas than corresponding unsupported preparations, and the areas of supported catalysts decrease less during reduction.[51] The surface area of unreduced, supported catalysts was greater than the sum of the areas of cobalt oxide-promoter complex plus kieselguhr; the areas of catalysts containing calcined and flux-calcined kieselguhrs were larger by about 8 percent and those with untreated kieselguhrs by about 20 percent.[52 53] Two explanations are possible: (1) The fine structure of the untreated kieselguhr stabilized the cobalt oxide-promoter complex at the time of precipitation; or (2) a fraction of the cobalt was attached to the kieselguhr by cobalt hydrosilicate bonds. The calcined and flux-calcined kieselguhrs, being less soluble than the untreated kieselguhrs, would undergo the bonding process to a smaller extent. Untreated kieselguhrs were more effective than calcined in maintaining surface area during reduction.

[51] Work cited in footnote 26, p. 7.
[52] Work cited in footnote 18, p. 4.
[53] Work cited in footnote 50, p. 20.

COBALT CARBIDE

PREPARATION AND IDENTIFICATION

Extended treatment of finely divided cobalt [54] with carbon monoxide at atmospheric pressure and 226° to 230° C. increased the carbon content to 9.3 percent, corresponding to the formula Co_2C. Under these conditions the reaction was slow and required about 500 hours for completion. The product reacted readily and completely with hydrogen at 240° to 250° C. to form α-cobalt and methane. When the carburization temperature was increased above 230° C., the reaction rate was increased, and the amount of carbon deposited was no longer limited to 9.3 percent. Instead, the carbon : cobalt ratio increased without apparent restriction as long as the metal was exposed to carbon monoxide. The product formed in this manner did not react completely with hydrogen at 240° to 250° C. A carbon residue remained that reacted with hydrogen only at temperatures

[54] Bahr, H. A., and Jessen, V., [Dissociation of Carbon Monoxide on Cobalt]: Ber. deut. chem. Gesell., vol. 63B, 1930, pp. 2226-2237.

above 350° C. but was not completely removed even at 620° C. The amount of carbon that could be hydrogenated at 240° to 250° C. never exceeded the theoretical amount (9.3 percent) for Co_2C. Thus, carbon could be deposited in two forms that were sharply differentiated by the temperature ranges in which they reacted with hydrogen. Samples carburized above 315° C. did not contain any appreciable amount of carbon capable of hydrogenation at or below 250° C. Bahr and Jessen [55] called this carbon "carbidic" carbon and the carbon capable of hydrogenation only above 350° C. "free" carbon. That the carbidic carbon actually forms cobalt carbide with a distinct crystal structure and not a terminal solid solution of carbon in α-cobalt is shown in the following work by the Bureau of Mines.[56]

Cobalt oxide was prepared by precipitation from cobalt nitrate solution with ammonium hydroxide. The X-ray diffraction pattern of the precipitate was identical with that of the pink cobaltous hydroxide described by Weiser and Milligan.[57] When the precipitate was heated at 150° C. for 24 hours it became black, and X-ray diffraction analysis showed it to be Co_3O_4, isomorphous with magnetite. The black oxide contained 68.9 percent cobalt. Samples of the oxide were reduced in hydrogen for about 80 hours at 300° C., to constant weight. During the reduction the color of the samples changed from black to bluish, metallic gray. Less than 0.3 percent oxygen remained after reduction. Carburization was carried out in a stream of carbon monoxide at a rate of about 1 liter per hour. Heating and cooling always took place in an atmosphere of nitrogen to avoid formation of cobalt carbonyl. After each stage of carburization or hydrogenation a sample was removed for X-ray analysis. Carbidic carbon was determined by hydrogenating the carburized sample at the temperature of carburization if this was less than 300° C. The weight ratios of total carbon, carbidic carbon, and free carbon to cobalt were calculated as follows:

$$(a)\quad \frac{\text{Weight of total carbon}}{\text{Weight of cobalt (reduced sample)}}=\frac{\text{Total carbon}}{\text{Cobalt}}; \tag{2}$$

$$(b)\quad \frac{\text{Weight loss on hydrogenation}}{\text{Weight of cobalt (reduced sample)}}=\frac{\text{Carbidic carbon}}{\text{Cobalt}}; \tag{3}$$

$$(a)-(b)=\frac{\text{Free carbon}}{\text{Cobalt}}. \tag{4}$$

The results are summarized in table 14. Carburization of cobalt leads to the formation of a new phase that reverted to the original α-cobalt upon treatment with hydrogen. This new phase could be a carbide or an allotrope of cobalt. The latter possibility was unlikely, because the new phase occurred only when carbon was present. The X-ray pattern could not have been due to carbon alone, because it does not have enough diffracting power to register on the photographic film in the same time as metallic cobalt. Furthermore, the diffraction lines of metallic cobalt disappeared as the new phase developed, suggesting that cobalt participated in its formation. That the new diffraction pattern was due to a single phase rather than two or more phases is indicated by the similarity of the patterns of all completely carburized samples prepared under various conditions. Figure 7 shows typical patterns obtained by X-ray diffraction. To investigate any diffraction lines that might be present at smaller angles than those found with the 71-mm. camera, a 114-mm. camera was used that was capable of resolving a reflection from an interplanar spacing of 20 A.; no new lines were found. The simplicity of the pattern, which is definitely noncubic, also suggested that it stemmed from a single phase, for if it were caused by 2 or more phases these phases would need to have even simpler patterns, and the possibility of 2 such simple patterns occurring simultaneously is slight. All these considerations point to the conclusion that carbidic carbon is combined with cobalt in a distinct crystalline phase with the diffraction pattern shown in table 15. Quantitative carburization and hydrogenation data suggest an approximate formula of Co_2C. An analysis of the structure of cobalt carbide was made by Drain and Michel,[58] who ascribed an orthorhombic structure to it and gave the lattice parameters as

$a=2.904$ A. $b=4.465$ A. $c=4.368$ A. $c/b=0.978$.

A slight variation of these parameters was found with the method of preparation, and this is thought to be due to small differences in the extent of carburization. Their measured and calculated data agree well with those of Hofer and Peebles (table 15).[59]

[55] Work cited in footnote 54, p. 21.
[56] Work cited in footnote 30, p. 9.
[57] Weiser, H. B., and Milligan, W. O., Transformation From Blue to Rose Cobaltous Hydroxide: Jour. Phys. Chem., vol. 36, 1932, pp. 722-734.
[58] Drain, J., and Michel, A. [Structure and Thermomagnetic Properties of Cobalt Carbide, Co_2C]: Bull. soc. chim., 1951, pp. 547-549.
[59] Work cited in footnote 30, p. 9.

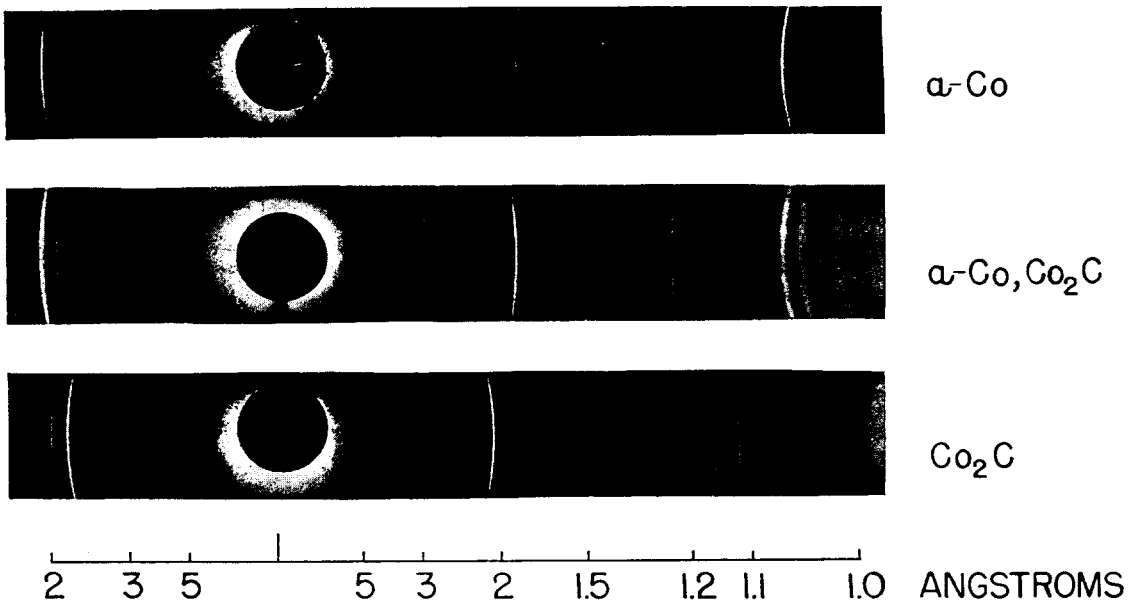


FIGURE 7.—Diffraction Patterns of Cobalt Metal, Partly Carbided Metal, and Cobalt Carbide as Obtained by Hofer and Peebles; Work Cited in Footnote 30.

TABLE 14.—*X-ray studies of carburized and hydrogenated cobalt*

Experiment	Carburization			Hydrogenation			X-ray diffraction analysis
	Temp., ° C.	Time, hours	Total carbon, percent	Temp., ° C.	Time, hours	Carbidic carbon, percent	
11	Original reduced sample						α-Co
	218	136	2.77				α-Co, Co_2C
	218	1,634	9.07				Co_2C
	218	1,634	9.13	218	149	8.50	α-Co
17	Original reduced sample						Do.
	243	93	6.29				α-Co, Co_2C
	243	448	10.69				Co_2C
	243	448	9.14	243	93.0	3.94	α-Co
18	266	20	5.33				Do.
	266	64	16.92				α-Co, Co_2C
	266	341	39.27				α-Co, Co_2C, C
	266	341	41.02	266	44	7.72	α-Co, C
16	Original reduced sample						α-Co
	292	47	5.33				Do.
	292	112	36.51				α-Co, C
	292	205	60.21				α-Co, Co_3O_4, C
19	390	7.8	21.0				α-Co
	390	12.7	32.64				α-Co, C
	390	24.3	46.39				Do.
	390	24.3	47.27	292	31.4	0.00	Do.

The formation of free carbon during the carburization of cobalt changed the color of the sample from gray to black. Carbon deposition was quite rapid at 292° C.; one sample (experiment 16, table 14) contained 60 percent carbon after carburization for 205 hours. The pressure from the accumulated carbon was sufficient to break the glass reaction tube after about 250 hours. Consequently, this sample was partly oxidized and produced the pattern of Co_3O_4 upon X-ray diffraction analysis.

TABLE 15.—*X-ray diffraction data for cobalt carbide*

I/I_1[1]	$d/n_{experimental}$[2,3]	$d/n_{experimental}$[2,4]	$d/n_{calculated}$[2,4]	I/I_1[1]	hkl[5]
----------	----------	4.55	4.36	vW	(001)
----------	----------	3.15	3.12	vW	(011)
W	2.4137	2.425	2.433	W	(110)
vW	2.3287	----------	----------	----------	----------
W	2.1712	2.176	2.184	vW	(002)
vS	2.1127	2.121	2.125	vS	(111)
vW	[6] 2.0358	----------	----------	----------	----------
S	1.9826	1.979	1.987	S	(021)
vW	[6] 1.9159	----------	----------	----------	----------
M	1.6244	1.626	1.624	W	(112)
vW	1.5558	1.558	1.56	vW	(022)
W	1.4454	1.452	1.452	W	(200)
M	1.3166	1.326	1.3245	W	(130)
M	1.2469	1.2485	1.248	W	(113)
W	1.2187	1.219	1.218	M	(023)
W	1.2053	1.208	1.2085	M	(202)
S	1.1680	1.173	1.1724	S	(221)
S	1.1267	1.132	1.132	S	(132)
vW	1.0754	1.091	1.090	W	(004)
vW	1.0638	----------	----------	----------	----------
vW	1.0565	----------	----------	----------	----------
M	.9949	----------	----------	----------	----------
vW	.9895	----------	----------	----------	----------

[1] Relative intensities: S=strong, M=medium, W=weak, v=very.
[2] Interplanar spacings in A.
[3] Burea of Mines data (footnote 30, p. 9).
[4] French data (reference 58, p. 22).
[5] Miller indices.
[6] α-cobalt line?

RATE OF CARBIDE FORMATION

Studies of the rate of carburization of a cobalt catalyst (catalyst 108B) showed a rapid initial rate, followed by a second stage in which the rate was constant; this in turn was followed by a period of decreasing rate, as shown in figure 8.[60] Although the results obtained by different

[60] Weller, S., Kinetics of Carbiding and Hydrocarbon Synthesis With Cobalt Fischer-Tropsch Catalysts: Jour. Am. Chem. Soc., vol. 69, 1947, pp. 2432-2436.

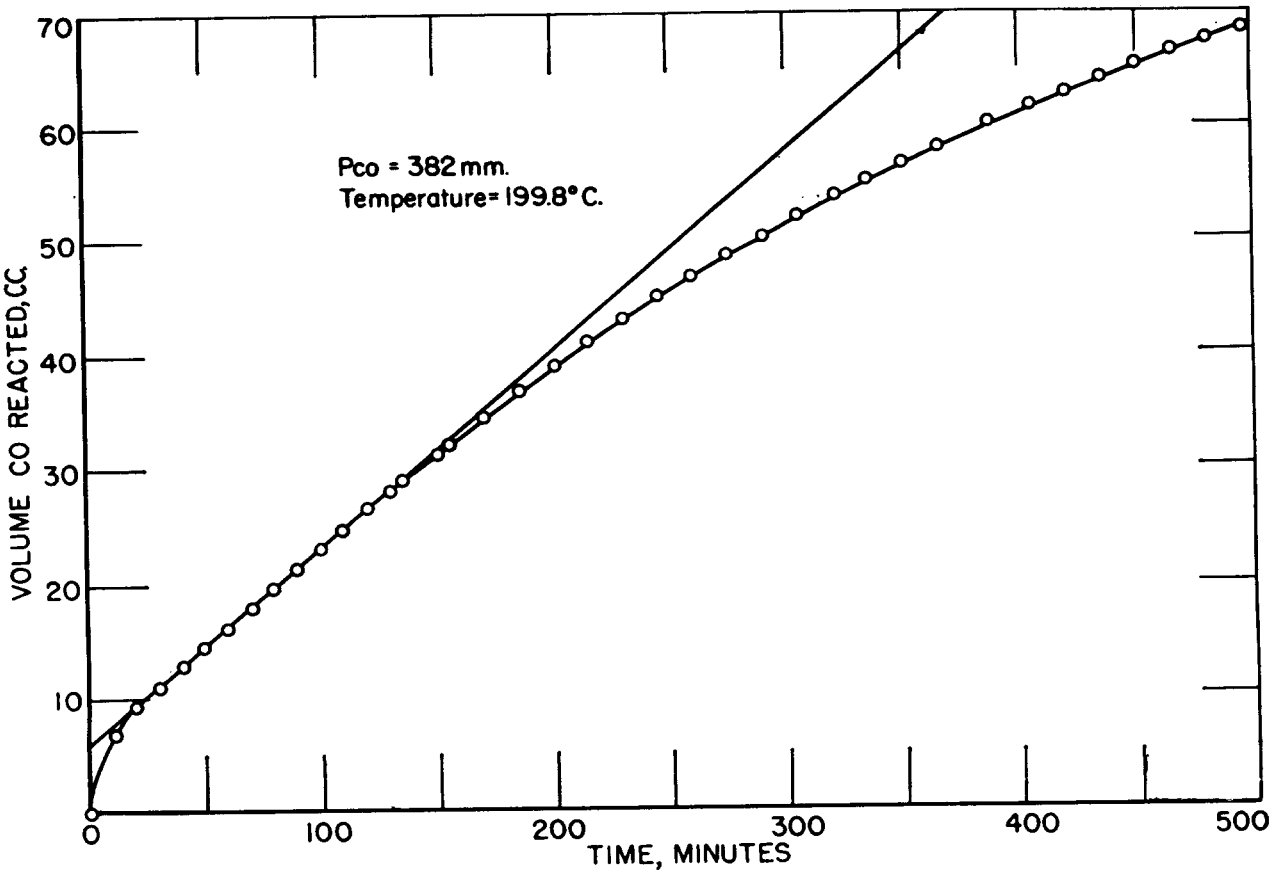


FIGURE 8.—Rate of Carburization of Cobalt-Thoria-Kieselguhr Catalyst 108B.

investigators are divergent, all data indicate that the rate of the second stage of carbiding is slower than the rate of synthesis. If the initial rapid rate of carbiding is greater than the rate of synthesis, then the carbon deposited as carbide at this stage may be an intermediate in the synthesis. Comparison of carbiding and synthesis rates, however, is not a very satisfactory way of testing the carbide hypothesis. For example, even if the synthesis does proceed by a carbide mechanism, the rates of carbiding and synthesis may depend upon different rate-controlling steps.

Cobalt might be oxidized by carbon dioxide according to two reactions:

$$CO_2 + Co = CoO + CO; \quad (5)$$

and

$$CO_2 + 2Co = 2CoO + C. \quad (6)$$

Reaction (5) can be excluded on a thermodynamic basis. Reaction (6), however, is thermodynamically possible. From data of Emmett and Shultz [61] for the reaction

$$CoO + H_2 = Co + H_2O, \quad (7)$$

and the data of Wagman and others [62] for the reactions

$$H_2 + 1/2O_2 = H_2O; \quad (8)$$

$$C + O_2 = CO_2, \quad (9)$$

the free energies for reaction (6) at 400°, 500°, and 600° K. were calculated to be −4.03, −0.49, and +3.04 kcal./mol, respectively. However, when carbon dioxide at atmospheric pressure was circulated over a reduced sample of catalyst 108B (cobalt-thoria-kieselguhr) at 150°, 200°, and 250° C. for at least 3 hours at each temperature, no reaction was observed, and the treated catalyst showed normal activity in the hydrocarbon synthesis.

FORMATION OF FREE CARBON

When cobalt carbide is hydrogenated or decomposed thermally at temperatures below about 360° C., hexagonal close-packed cobalt is formed. This fact is useful in tracing the origin of metallic cobalt in the catalyst.[63] [64]

[61] Emmett, P. H., and Shultz, J. F., Equilibrium in the System Co-H_2O-CoO-H_2. Free-Energy Changes for the Reaction $CoO + H_2 = Co + H_2O$ and the Reaction $Co + \frac{1}{2}O_2 \gtrless CoO$: Jour. Am. Chem. Soc., vol. 51, 1929, pp. 3249-3262.

[62] Wagman, D. D., Kilpatrick, J. E., Taylor, W. J., Pitzer, K. S., and Rossini, F. D., Heats, Free Energies, and Equilibrium Constants of Some Reactions Involving O_2, H_2, H_2O, C, CO, CO_2, and CH_4: Jour. Research, Nat. Bureau of Standards, vol. 34, 1945, pp. 143-161.

[63] Hofer, L. J. E., and Peebles, W. C., X-ray Diffraction Studies of the Action of Carbon Monoxide on Cobalt-Thoria-Kieselguhr Catalysts. I: Jour. Am. Chem. Soc., vol. 69, 1947, pp. 2497-2500.

[64] Hofer, L. J. E., Peebles, W. C., and Bean, E. H., X-ray Diffraction Studies of the Action of Carbon Monoxide on Cobalt-Thoria-Kieselguhr Catalysts. II: Jour. Am. Chem. Soc., vol. 72, 1950, pp. 2698-2701.

The results of carburization of reduced catalyst 108B between 208° and 298° C. (table 16 and fig. 9) show that the carburized product changes progressively from one containing only cobalt carbide (up to 243° C.) to one containing only disordered cobalt as the carburizing temperature was increased from about 243° to 298° C. No hexagonal cobalt was observed. The amount of carbide found at the end of the carburizing period was therefore a maximum, because any cobalt carbide decomposing into cobalt metal would have formed hexagonal and not disordered cobalt.[65] [66] Table 16 also indicates that only as much carbidic carbon as had been removed by hydrogenation could be reintroduced into a catalyst by recarburization at 220° C., because free carbon, either by poisoning or by mechanical blocking, had made certain portions of the catalyst inaccessible to carbiding.

Figure 10 shows the effect of carburization temperature on successive carburizations. A sample of reduced catalyst 108B was carburized (with carbon monoxide) at 208°, 258°, and 298° C. After each carburization carbidic carbon was removed by hydrogenation at 208° C. About 10 grams of carbidic carbon per 100 grams of cobalt was introduced by carburization at 208° C. Carburization at 258° C. produced the same amount of carbidic carbon, but some free carbon was also formed.

[65] Weller, S., Hofer, L. J. E., and Anderson, R. B., Role of Bulk Carbide in the Fischer-Tropsch Synthesis: Jour. Am. Chem. Soc., vol. 70, 1948, pp. 799-801.

[66] Hofer, L. J. E., Cohn, E. M., and Peebles, W. C., Isothermal Decomposition of the Carbide in a Carburized Cobalt Fischer-Tropsch Catalyst: Jour. Phys. and Colloid Chem., vol. 53, 1949, pp. 661-669.

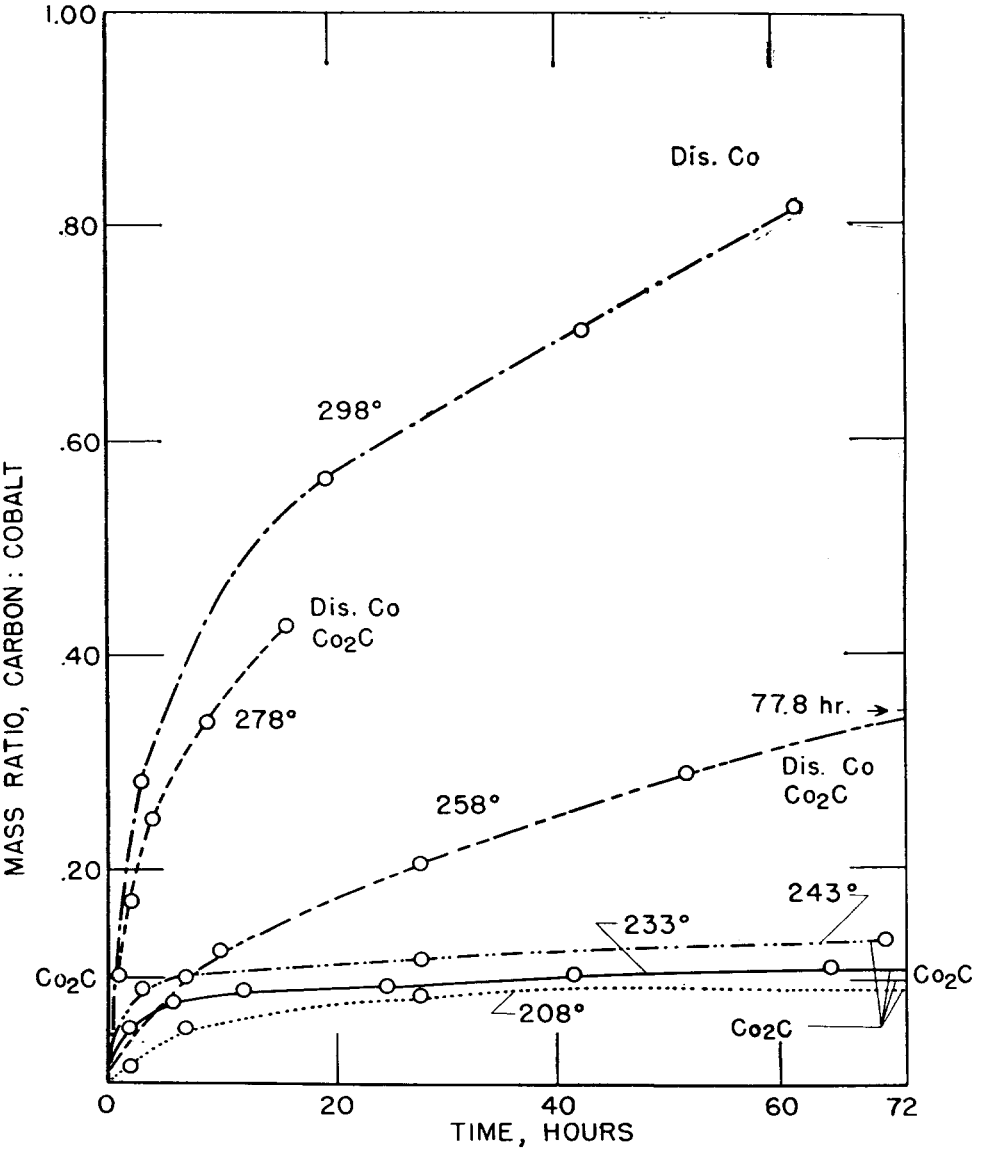


FIGURE 9.—Carburization of Cobalt-Thoria-Kieselguhr Catalyst 108B With Carbon Monoxide in the Temperature Range 208°–298° C.

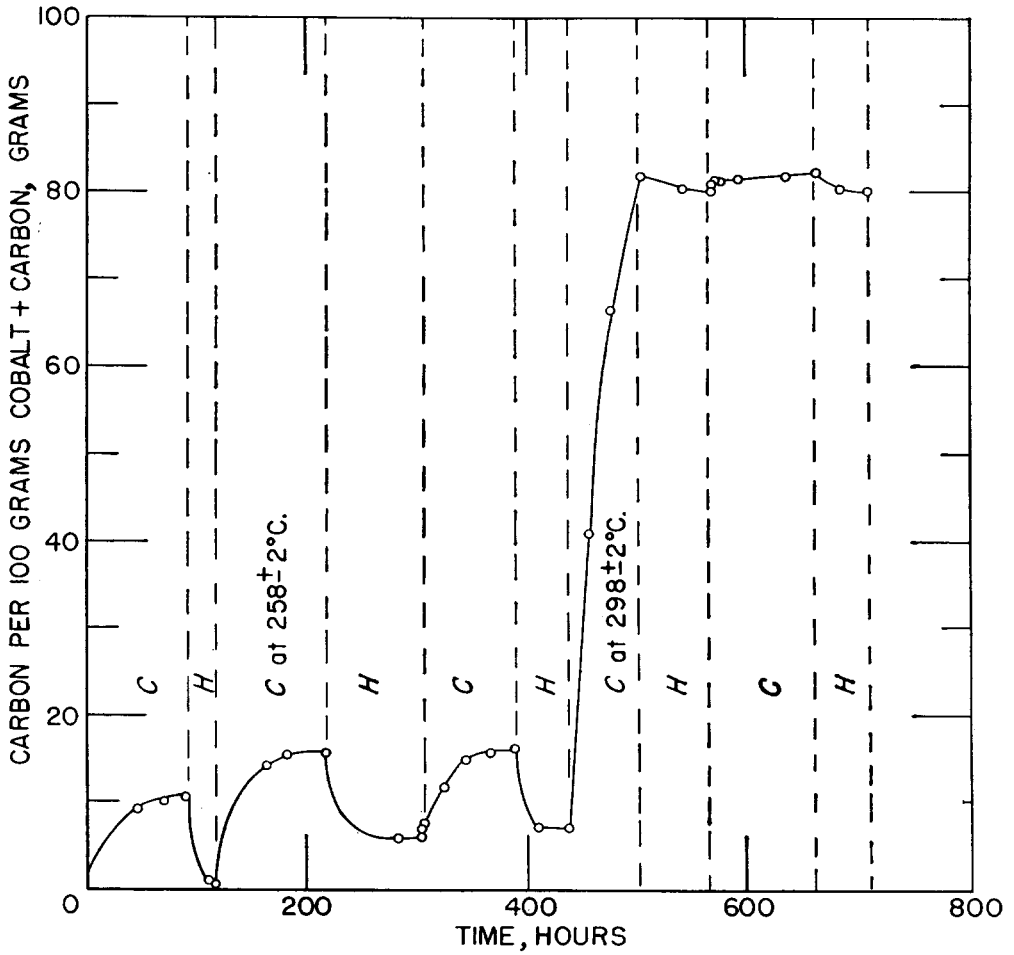


FIGURE 10.—Effect of Temperature of Carburization Upon Subsequent Carbide Formation; Catalyst 108B: *C*, Carburization; *H*, hydrogenation, all at 208±2° C., except as noted.

TABLE 16.—*Carbon deposition on cobalt-thoria-kieselguhr catalyst 108B*

(Reduced in hydrogen at 400° C.)

Experiment No.	Carburization [1]		Product (by X-ray diffraction)	Weight ratios		
	Temp., ° C.	Time, hours		C:Co total	C:Co carbidic [2]	C:Co recarbided [3]
24	298	62	Disordered Co	0.820	0.017	0.008
31	278	15	Disordered Co+Co_2C.	.435	.054	
23	258	77.8	Disordered Co+Co_2C.	.352	.063	.089
37	243	70.6	Co_2C	.138		
33	233	112	Co_2C	.120	.099	
27	208	120.8	Co_2C	1.04	1.04	.099

[1] Catalysts carburized in pure CO at atmospheric pressure and a space velocity of 100 $hr.^{-1}$

[2] Amount of carbon that could be removed by treating with hydrogen at temperature of carbon deposition.

[3] Amount of carbidic carbon that could be added by CO treatment at 220° C.

On recarburization at 208° C. only 9.2 grams of carbidic carbon per 100 grams of cobalt was introduced. Carburization at 298° C. resulted in the formation of only 2.1 weight-percent carbidic carbon based on cobalt. Thus, free carbon inhibited the formation of carbidic carbon, and carburizing at temperatures at which free carbon was deposited inhibited carbide formation not only at those temperatures but poisoned the catalyst toward subsequent formation of carbide under favorable temperature conditions.

THERMAL STABILITY OF COBALT CARBIDE

The isothermal decomposition of cobalt carbide in a carburized catalyst was studied by means of a magnetic balance, and the results were supplemented by a chemical method.[67] The following equation represents the decomposition reaction:

$$Co_2C \longrightarrow 2\alpha\text{-}Co + (\text{free})C. \qquad (10)$$

Catalyst 108B was reduced and carbided to a weight ratio of 0.1003 gram of carbon per gram of cobalt (theoretical for Co_2C=0.1017).

[67] Work cited in footnote 66 ,p. 25.

The carburized catalyst showed only the X-ray diffraction pattern of cobalt carbide. Samples in evacuated, sealed glass ampoules were placed in the magnetic balance, and the force of the magnetic field on the samples was measured at room temperature. They were then heated in situ as rapidly as possible to the reaction temperature, at which they were maintained while the force was measured periodically. Decomposition rates were measured at 300°, 325°, 335°, 345°, 355°, and 359° C. Figure 11, a typical experimental curve obtained at 345° C., shows the magnetic moment as a function of time. The paramagnetic or weakly ferromagnetic carbide underwent a transition to strongly ferromagnetic metal. That this transition was actually a decomposition into free carbon and cobalt was shown by X-ray diffraction analysis.

The measured change in the magnetic force experienced by a sample during thermal treatment was converted to percentage of cobalt carbide by making the following assumptions:

1. The initial magnetization of the sample was due to free cobalt. Although the X-ray patterns of the carbided catalysts showed only lines for cobalt carbide, the presence of metallic cobalt cannot be excluded solely on this basis. The initial magnetic moment could be caused by the presence of 6 to 7 percent of free metallic cobalt, the corresponding quantity of carbon being present as free carbon.

2. The force was directly proportional to the amount of cobalt present. Although this cannot be strictly true, the actual quantity of nonferromagnetic cobalt present

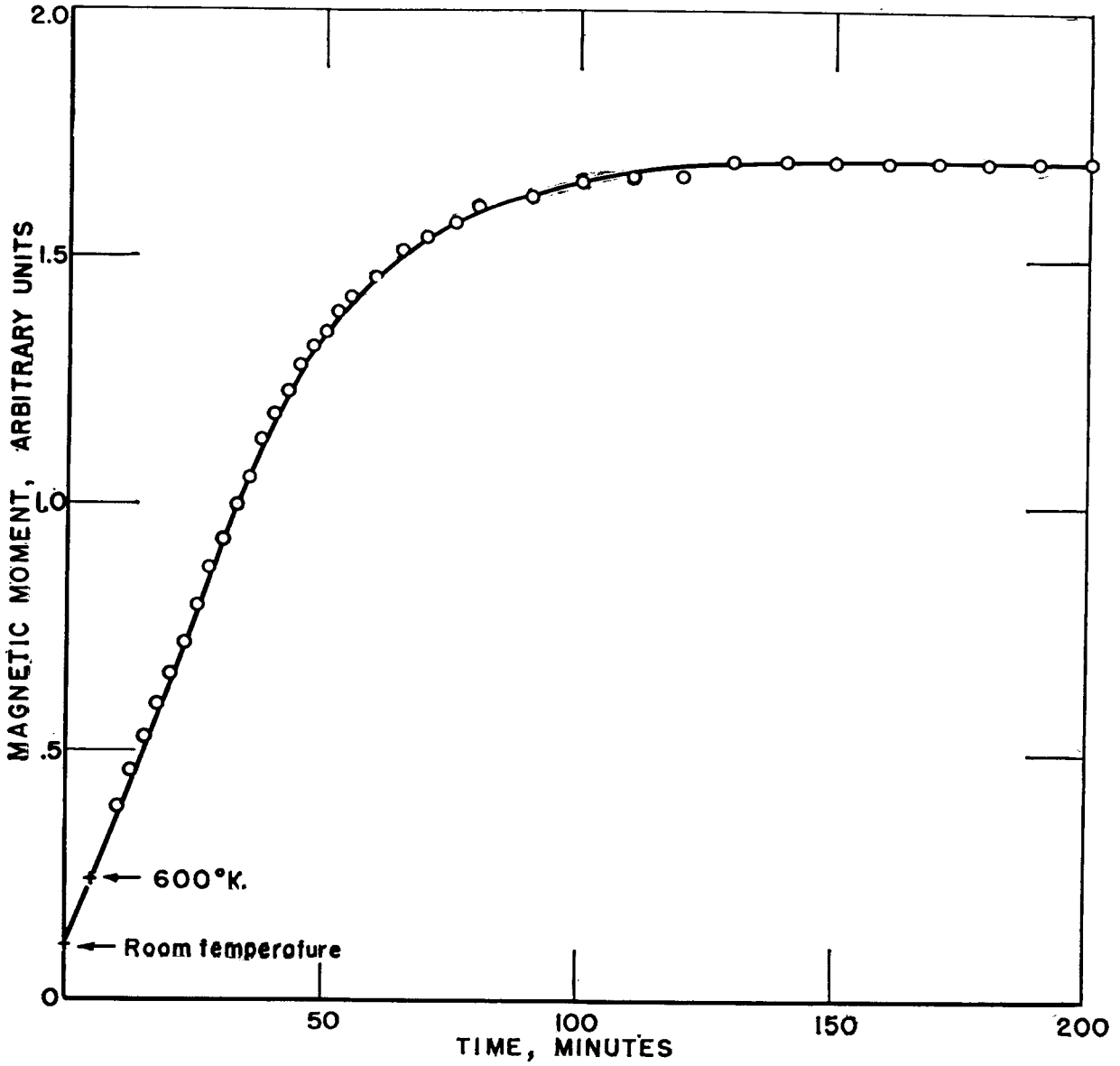


FIGURE 11.—Thermal Decomposition of Carbided Cobalt Catalyst 108B in Magnetic Balance at 618° K.

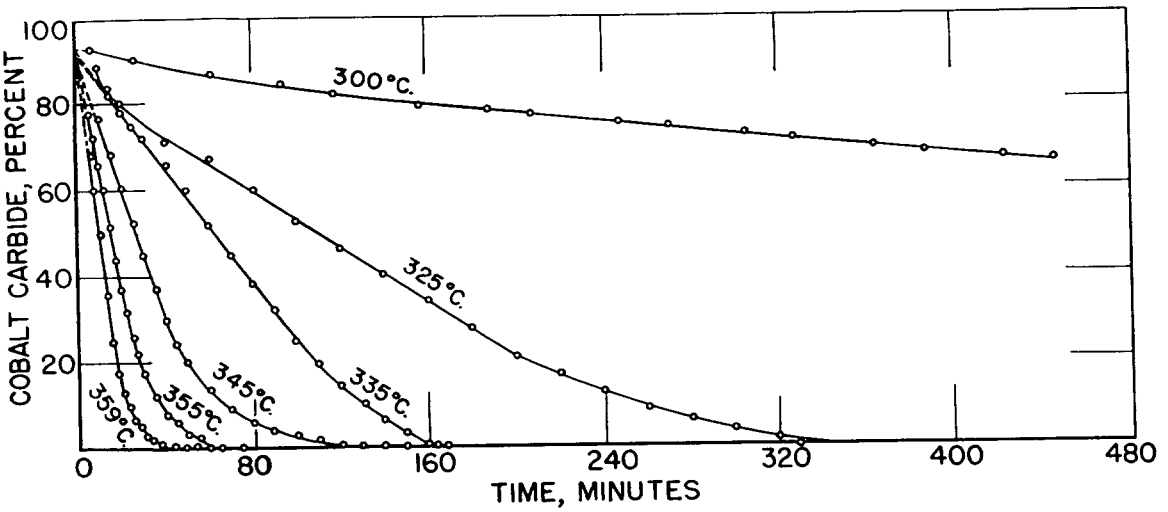


FIGURE 12.—Isothermal Decomposition of Carbide in Carbided Cobalt Fischer-Tropsch Catalyst 108B.

(small aggregates) was within the limit of error of the measurement, as shown by the chemical experiments. The results are summarized in figure 12, where the percentage of cobalt carbide remaining in the sample is shown as a function of time, with temperature as parameter. From carbide contents of 80 to 25 percent the decomposition appeared to be zero order. Calculation of the specific reaction rate constants in this range and application of the Arrhenius equation yielded an apparent over-all activation energy of 54.3 kcal./mole. The results obtained with the magnetic balance were verified by purely chemical experiments in which the quantity of cobalt carbide (remaining after heat treatment in nitrogen) was determined by the change in weight of partly decomposed samples upon hydrogenation. It was evident from the results that the magnetic method gave a true indication of the amount of metallic cobalt present, that the quantity of nonmagnetic cobalt was negligible, and that nitrogen had no effect upon the thermal decomposition of the carbide.

In an extension of these studies, Drain and Michel [68] found that the rate of decomposition depended strongly upon the method of preparing the catalyst. Unsupported, unpromoted cobalt carbide appeared to contain less carbidic carbon and to be more resistant to decomposition than preparations made with 10 and 18 percent thoria. They also observed that a sample containing 10 percent thoria, decomposing in vacuum between 260° and 310° C., formed a ferromagnetic hexagonal close-packed phase (a=2.514 A., c=4.098 A., c/a=1.630) which decomposed further into pure cobalt and carbon between 448° and 498° C. No such intermediate solid solution of carbon in cobalt was observed by Hofer and Peebles [69] during carburization of cobalt or by Hofer, Cohn, and Peebles [70] during isothermal decomposition of cobalt carbide as formed in a cobalt-thoria-kieselguhr catalyst.

[68] Work cited in footnote 58, p. 22.
[69] Work cited in footnote 30, p. 9.
[70] Work cited in footnote 66, p. 25.

IRON CATALYSTS

In contrast to cobalt catalysts, for which the only really successful preparations consist of promoted cobalt basic carbonate precipitated on kieselguhr, effective iron catalysts can be prepared in a variety of ways. This section describes the preparation and properties of precipitated-, fused-, and cemented-iron catalysts, as well as preparations made by simple treatment of inexpensive iron ores and industrial byproducts. The reduction of catalysts in hydrogen and the preparation of carbides, nitrides, and carbonitrides of iron are also considered.

PREPARATION

PRECIPITATED CATALYSTS

Some precipitated-iron catalysts made by the Bureau of Mines have been described previously, and methods for their preparation have been discussed.[71] More recently, a series of precipitated catalysts (P3003) containing 100Fe : 10Cu : 0.5K_2CO_3 has been prepared.

Ferric nitrate and cupric nitrate were dissolved in enough water to make an approximately 0.56 molar solution. Enough 1.0 molar sodium carbonate solution was made to provide the stoichiometric quantity for the nitrates plus 10 percent in excess. About 80 percent of the sodium carbonate solution was added to the nitrate solution at room temperature. After this mixture was heated to 70° C. the remaining carbonate solution (heated to boiling) was added to it to precipitate the iron and copper. The resultant slurry was boiled a short time and filtered. The precipitate was washed with hot water until the washings showed a negative

[71] Storch, H. H., Anderson, R. B., Hofer, L. J. E., Hawk, C. O., Anderson, H. C., and Golumbic, N., Synthetic Liquid Fuels From Hydrogenation of Carbon Monoxide, Part I: Bureau of Mines Tech. Paper 709, 1948, 213 pp.

test for nitrate with sulfuric acid-diphenylamine solution. Excess water was removed by a suction filter. The moist filter cake was mixed with water to form a smooth slurry. Sufficient 0.1 molar potassium carbonate solution was then added to give the desired alkali content. The mixture was agitated until homogeneous, dried at 105° to 110° C., and either crushed to a specified mesh size or pelleted. When the catalyst was supported on kieselguhr, the carrier was mixed with the moist precipitate before alkali addition.

FUSED-MAGNETITE CATALYSTS

One of the objectives of the Bureau of Mines catalyst-testing program is development of catalysts that are strong enough to withstand the rigorous conditions of operation of modified Fischer-Tropsch processes, such as the oil-circulation process.

Commercial fused-iron catalysts fulfill many of the requirements for mechanical strength and stability. The German synol catalyst obtained from the Leuna plant of I. G. Farbenindustrie is somewhat typical of ammonia-synthesis catalysts prepared in Germany. Usually these were made by burning iron in oxygen and adding aluminum and potassium oxides to the molten oxide. Commercial American ammonia-synthesis catalysts usually are prepared by fusing magnetite in an electrical conduction furnace. Catalysts D3004, D3005, D3007, D3008, D3001, and D3006 (p. 37) are typical American ammonia-synthesis catalysts. The Bureau of Mines procedure for preparing fused catalysts by burning iron in oxygen follows:

Powdered electrolytic iron (Plastiron) was oxidized and melted in oxygen, and dry promoters were added to the partly fused mass. The promoter mixture was prepared as follows: A slurry of alumina (Norton "RR" alundum, alkali- and carbon-free) was prepared in a solution of potassium nitrate and evaporated to dryness over a steam bath. The iron was melted as follows: A steel container, having walls of ½-inch thickness, was lined with reagent-grade ferric oxide that had been previously heated to 600° C. This oxide formed a layer on which iron could be melted without affecting the steel container or introducing impurities into the melt. A quantity of the pure iron was placed in the container on the surface of the iron oxide and heated by means of an oxyhydrogen blowpipe flame directed at the center of the iron mass. When the center became molten, a rapid stream of pure oxygen was directed on the heated portion of the iron. The heat of the reaction ($3Fe+2O_2 \rightarrow Fe_3O_4$) was sufficient to melt both remaining iron and iron oxide. The mass remained molten under the flow of oxygen for a short time, until oxidation and fusion were complete or nearly complete. When approximately a third of the iron was melted, the powdered alumina-alkali promoter mixture was added. After the fusion was complete, the catalyst was cooled and broken to the desired particle size.

The preparations of fused catalysts of this type are included in table 17.

A practical method for preparing small batches of catalyst by the electrical fusion method was developed at the Bureau of Mines laboratories. The fusion furnace is shown in figure 13. The trough was coated with moist magnetite ore and dried. The catalyst material, magnetite plus promoters, was placed in the trough, and an iron rod (¼ inch in diameter) was inserted between the water-cooled electrodes. The voltage applied to the electrodes was controlled by an inductance reactor. As the voltage was increased, the iron rod melted, forming a conducting medium to carry the current until enough magnetite had melted. As the melting proceeded the unfused magnetite-promoter mixture was pushed into the area between the electrodes with a wooden stick.

After about 3 hours—the time depending upon the desired amount of molten material—the current was turned off and the material permitted to cool. The pig of fused material was removed, and the adhering nonfused mixture was separated with a hammer and a wire brush. The pig was then broken into smaller pieces with a hammer, and these pieces were reduced to the desired size in a roller mill. The crushed material was sieved to the desired mesh size. Fines could be incorporated into subsequent batches by adding them to the fusion mixture. In the apparatus shown in figure 13, pigs weighing 4 to 5 pounds were prepared. Alkali as potassium hydroxide, carbonate, or nitrate may be incorporated into the fusion mixture, or it may be added subsequently by immersing the catalyst in a solution of the potassium compound. In the latter method the amount of alkali retained by the catalyst depends upon the concentration of the solution in which it is immersed. In the ammonia synthesis the method of alkali addition produces no differences in the resulting activity of the catalysts. This appears to be the case in the Fischer-Tropsch synthesis; however, the effect has not been thoroughly investigated. Table 18 describes several fused catalysts prepared by this method.

Two fused catalysts were prepared by variations of the thermite process. These catalysts were very hard and had a large proportion of macropores. Details of the preparations were:

A3208–1.—Pure magnetite (2,400 grams) was thoroughly mixed with 240 grams of reagent-grade

aluminum-metal powder and then blended with 600 grams of finely powdered (less than 325-mesh) sponge iron, free from oxide. The mixture was heated to red heat in an iron dish. Reaction was then initiated by heating with an oxyhydrogen flame. After the evolution of heat diminished, the mass was cooled and broken to the desired mesh size. The particles were impregnated with a potassium carbonate solution to give the composition 100Fe : $1K_2O$.

A3209.—The thermite reaction was also used for this preparation. One kilogram of pure magnetite was mixed with 100 grams of aluminum powder and enough potassium carbonate to give the ratio 100Fe : $0.5K_2O$. The mixture was placed in a covered evaporating dish and heated to 900° C. to start the reaction. The hard cake that resulted was broken to the required mesh size.

CEMENTED CATALYSTS

So-called "cemented" catalysts were prepared by mixing the iron oxide with a binding agent, such as aluminum nitrate, and then heating the mixture to drive off the oxides of nitrogen. These catalysts are distinguished from sintered catalysts, in that a binding agent is used and that the active component is not drastically modified by heat. In most of the Bureau of Mines research finely divided iron oxides were used in preparing cemented catalysts. A very useful starting material was Alan Wood magne-

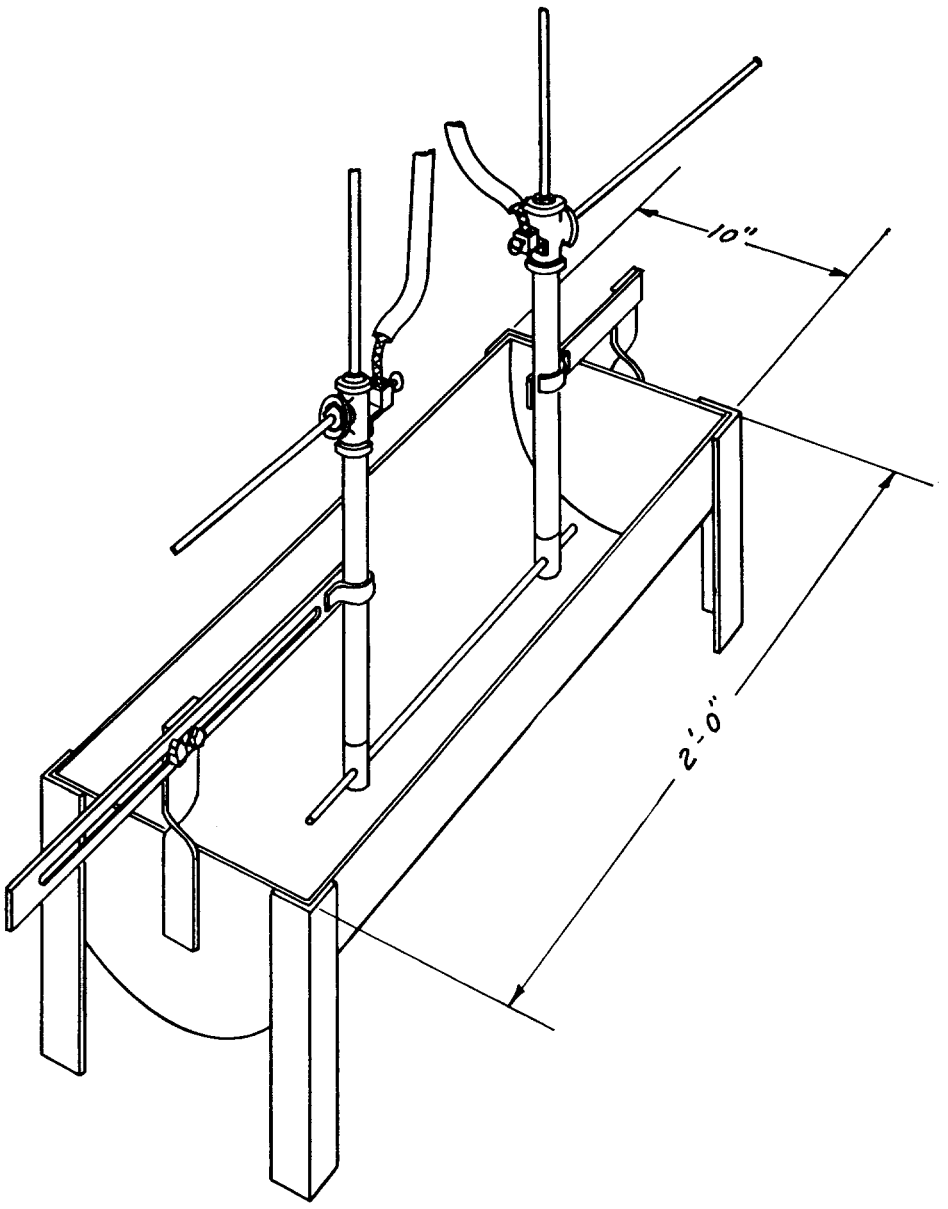


FIGURE 13.—Bureau of Mines Apparatus for Preparing Fused Catalysts.

TABLE 17.—*Preparation of fused-iron catalysts*

Catalyst	Materials			Preparation sequence	Purpose
	Iron	Alkali	Others		
A3212	Plastiron-powdered electrolytic iron.	KNO_3	Al_2O_3 (Norton alundum).	Alkali (KNO_3) and alumina made into paste and evaporated to dryness. Iron melted and oxidized on iron oxide layer, promoter added, fused mass cooled.	To duplicate German synol catalyst.
A3217	do	do	Powdered, activated alumina.	Iron mixed with powdered promoters, heated at 900° C. for 1 hr., then fused as A3212.	Do.
A4900	do	do	Al_2O_3, $CaCO_3$	do	Do.
L3011	Catalyst D3001 plus 30 percent iron.			Powdered catalyst and iron were mixed and fused as A3212.	Do.
A1000	Plastiron-powdered electrolytic iron.	None	None	Same as A3212 with alkali and alumina omitted.	To prepare a fused catalyst containing no structural promoter.
A2100	Catalyst A1000	K_2CO_3 solution.	None	Catalyst impregnated with enough K_2CO_3 solution to give desired alkali content. Dried at 105° C. and heated at 150° C.	Do.
D3004.1	Catalyst D3004	None	None	D3004 extracted with water in Soxhlet extractor for 65 hr.	To reduce alkali content of original catalyst.
P3003.262	Precipitated Fe_2O_3-CuO-K_2CO_3 catalyst was used.	None	None	Fused with oxyhydrogen torch on a layer of iron oxide.	Do.

tite, a high-purity ore obtained by magnetic separation by the Alan Wood Steel Co. For use in conventional blast furnaces the Alan Wood magnetite was formed into aggregates by forcing an aqueous slurry of the ore through a die attached to a high-frequency vibrator and sintering the compacted material into rough spheres at 1,200° C. in a rotating kiln. These rough spheres, called "glomerules," were active catalysts after crushing to a suitable particle size, alkali addition, and reduction but lacked mechanical strength. Crushed glomerules were converted to stronger particles by impregnating with bonding agents and heating. Table 19 describes preparations from Alan Wood magnetite. Cemented catalysts from various iron sources (table 20) and crushed glomerules are described later in this section. More complete

TABLE 18.—*Preparation of fused-iron catalysts by electrical fusion*

Catalyst	Materials			Preparation
	Iron	Alkali	Others	
P2007	Magnetite		3 percent Al_2O_3	Alan Wood magnetite mixed with alumina and fused in electrical conduction furnace.
A3207	Catalyst P2007	KNO_3 solution		P2007 impregnated with KNO_3 solution; dried at 105° C.
L3012	Magnetite		Silica, TiO_2, $KMnO_4$	Components mixed and fused as for P2007.
L3016	do	K_2CO_3 solution	20 percent MnO_2	Alan Wood magnetite mixed with manganese dioxide and fused in electrical conduction furnace. Impregnated with K_2CO_3 solution, as in A3207.

TABLE 19.—*Preparation of cemented-iron catalysts*

Catalyst	Materials			Preparation	Heat treatment
	Iron	Alkali	Others		
A3213.24	Alan Wood magnetite.	KNO_3	$Al(NO_3)_3$	Magnetite added to solution of $Al(NO_3)_3$ and KNO_3, evaporated to dryness with stirring.	16 hr. at 150° C. 16 hr. at 500° C.
A3218.087	do	K_2CO_3	$Al(NO_3)_3$	Magnetite impregnated with $Al(NO_3)_3$ and evaporated to dryness with stirring. Crushed to size and impregnated with alkali and dried.	16 hr. at 150° C.
A3211	do	KNO_3	$Al(NO_3)_3$	Same as A3213.24	16 hr. at 900° C.
A3215	do	KNO_3	$Al(NO_3)_3$	do	16 hr. at 150° C.
A3214	do	KNO_3	$Al(NO_3)_3$	do	Do. 16 hr. at 500° C.
A3220	Magnetite glomerules.	KNO_3	$Al(NO_3)_3$	Glomerules impregnated with solution of nitrates and evaporated to dryness.	16 hr. at 150° C. 16 hr. at 600° C.
L1002.2	Alan Wood magnetite.	$Na_2B_4O_7$		Borate solutions added to magnetite, evaporated to dryness with stirring.	15 hr. at 150° C. Crushed to size and 15 min. at 800° C.
L1004	do	$K_2B_4O_7$			Heated at 1,000° C. in forming glomerules.
L1006.11	do	$Na_2B_4O_7$		Same as above. Catalyst formed into glomerules.	
L1017	do				
L1019	Crushed glomerules.	$Na_2B_4O_7$		do	Do.
A3811	Reduced glomerules.	$Na_2B_4O_7$		Glomerules impregnated with solution of borax and all dried under CO_2 to prevent oxidation.	Catalyst reduced in hydrogen at 400° C. before use.
A3310	Alan Wood magnetite.	Potassium silicate.		Magnetite mixed with solution of silicate. Evaporated to dryness.	16 hr. at 150° C. Crushed to size. Samples heated under following conditions: (*a*) 16 hr. at 500° C., hard magnetic. (*b*) 16 hr. at 900° C., hard, nonmagnetic. (*c*) 16 hr. at 1,100° C., soft, nonmagnetic. (*d*) No heat treatment, soft, magnetic.
L1010.2	do	Sodium silicate.		do	15 min. at 800° C.
L1016	do	do		do	16 hr. at 500° C.
L2009	do	K_2CO_3 dextrin.		Magnetite mixed with dry K_2CO_3 and dextrin. Water was added to form a paste. Glomerules were formed.	Dried at 90° C.

preparative methods for four cemented catalysts follow.

A3213.24.—Aluminum nitrate solution (1,590 ml. containing 0.0136 gram of Al_2O_3 per milliliter of solution) was placed in an evaporating dish, and 18.52 grams of potassium nitrate was added. The solution was agitated with a mechanical stirrer while being heated, but not boiled, on a steam bath. Powdered magnetite (2,000 grams) was slowly added, with constant stirring. After addition of the magnetite the mixture was stirred for several minutes. The solution was evaporated with mechanical stirring until this was no longer practicable. It was then stirred manually until the mixture was dry. The dry mass was heated at 150° C. for 16 hours, then at 500° C. for 16 hours, broken into granules, and sieved. The granules were magnetic and moderately hard.

L1002.2.—A solution of borax ($Na_2B_4O_7.10H_2O$) in distilled water was prepared, containing a quantity of borax equal to 5 percent of the weight of the magnetite used. The volume of the solution was about twice that of the magnetite. The borax solution was added to the magnetite and the mixture was evaporated, with stirring, over a steam bath until a thick paste was obtained. This paste was dried 15 hours at 150° C. The cake was broken into granules of 6- to 10-mesh, which were heated at 800° C. for 15 minutes. Heating at lower temperatures produced soft granules that disintegrated in water.