SYNTHETIC LIQUID FUELS FROM HYDROGENATION OF CARBON MONOXIDE

Cobalt and Iron Catalysts for the Fischer-Tropsch Synthesis: Preparation and Characterization of Catalysts, Synthesis Tests, and Reaction Mechanism

(PART 2 of TWO PARTS)

By J. F. Shultz, L. J. E. Hofer, E. M. Cohn, K. C. Stein, and R. B. Anderson

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Preface

This is the second report on laboratory studies of the Fischer-Tropsch synthesis. The first (Bureau of Mines Technical Paper 709) contains a review of the literature and results of the Bureau's research on cobalt and iron catalysts through 1946. The present bulletin completes the account of studies of cobalt catalysts and summarizes work on iron catalysts through 1953.

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J. F. Shultz,[2] L. J. E. Hofer,[2] E. M. Cohn,[3] K. C. Stein,[2] and R. B. Anderson [4]

Summary

AMONG the more important results of the study of cobalt Fischer-Tropsch catalysts, reported in this bulletin, are the unusual X-ray diffraction patterns obtained with precipitated, reduced-cobalt catalysts. These patterns indicate that the metal has a disordered layer structure that represents a hybrid between the face-centered cubic and the hexagonal close-packed modifications of cobalt. Carburization to cobalt carbide and subsequent reduction result in development of the hexagonal close-packed cobalt structure. Since only the hybrid structure has been found in active, used catalyst, bulk cobalt carbide cannot be an intermediate phase in synthesis. Furthermore, cobalt carbide is not an active phase in synthesis, because its activity is very low compared with that of metallic cobalt. In synthesis at atmospheric pressure most of the synthesis product passes from the catalyst bed as vapors, and high-molecular-weight hydrocarbons accumulate and eventually block the pores of the catalyst. At higher pressures a sizable fraction of product flows as liquid from the catalyst bed. Thus, the pores are almost immediately filled with hydrocarbons, and the composition of material in the pores and of liquid flowing over the catalyst is essentially the same.

In contrast to cobalt catalysts, which are prepared successfully only by precipitation on a carrier, active iron catalysts can be prepared by a variety of methods, such as precipitation, fusion, sintering, and cementation. Also, precipitated catalysts and those containing oxides that have not been heated at high temperatures need not necessarily be reduced before synthesis but can be pretreated in synthesis gas or carbon monoxide. This bulletin contains extensive data on catalytic and other properties of iron carbides, nitrides, and carbonitrides. In contrast to cobalt and nickel carbides, carbides of iron, as well as iron nitrides and carbonitrides, are active in the synthesis. Iron nitrides and carbonitrides are shown to have advantages over reduced- as well as carbided-iron catalysts in activity, life, and selectivity. Iron nitrides are rapidly transformed to carbonitrides in the synthesis, and the behavior of nitrided catalysts may be attributed to the presence of carbonitride phases. The products from iron carbonitrides contain more material boiling in the gasoline range and less heavy oil and wax than those from iron carbides. A much larger amount of the product from carbonitride is oxygenated material, primarily ethanol and higher alcohols.

Effects of methods of preparation, carriers and promoters, pretreatment of catalysts, and variation of operating conditions on both catalysts and prod-

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ucts are reported.   Alkali as potassium oxide or carbonate appears to be the only important additive in determining the selectivity and activity of iron catalysts; however, other promoters or supports may be desired for improving the mechanical properties.   On the basis of experimentally observed product distributions, a mechanism is postulated to account for chain growth of products during synthesis.   Oxygenated, organic adsorption complexes on the catalyst surface are assumed to be intermediates in the formation of Fischer-Tropsch products.   A set of mathematical expressions is derived to predict not only the distribution of numbers of carbon atoms per molecule in the products but also the extent and kind of branching to be expected for each molecular size.

The appendix describes some equipment and techniques developed in the course of this work and gives a detailed account of the application of magnetic measurements to studies of ferromagnetic catalysts.

INTRODUCTION

Systematic studies of the Fischer-Tropsch synthesis were begun in Germany about 1925, following the basic discovery that the hydrogenation of carbon monoxide on metals of the iron group—cobalt, nickel, and iron—produced higher hydrocarbons and oxygenated molecules. In 1935 the results of German laboratory and pilot-plant experiments indicated that only cobalt catalysts were adequately developed; and, despite the scarcity and high cost of this metal, cobalt catalysts were employed in the German commercial synthesis plants in 1937–44. However, the inadequacies of both the catalyst and the commercial reactors were realized, and research on iron catalysts and more efficient reactors was continued. One goal of the catalyst development was to obtain a suitable iron catalyst for replacing cobalt in the existing commercial synthesis units. In 1943 comparative tests, the Reichsamtversuch, at Schwarzheide-Ruhland, demonstrated that remarkable progress had been made on iron catalysts. Advantages of iron catalysts include a wider range of selectivity and operating conditions, more valuable products containing (under some conditions) large yields of olefins and oxygenated material, and the use of inexpensive, available materials for catalyst preparation.

Although the principal investigations of the Fischer-Tropsch synthesis before 1944 were made in Germany, important research has been conducted in Great Britain from 1930 to the present time and in Japan from 1930 to 1945. After an early period of research (1926–30) a program of catalyst and reactor development was begun at the Bureau of Mines in 1942. Since 1944 several large American laboratories have investigated catalysts and reactor design, with special emphasis on fluidized synthesis processes with iron catalysts. One large synthesis plant is now on stream—the Sasol plant in the Union of South Africa. Severe operating difficulties have been experienced with entrained catalyst reactors in early operation of this plant; however, recent reports indicate that most of these difficulties will be solved in the near future. This plant also employs improved fixed-bed reactors recently developed in Germany.

In the Bureau of Mines catalyst studies from 1944 to 1947 emphasis was placed principally on studies of cobalt catalysts to provide a basic background on a fairly well developed catalytic system. Since 1947 investigations have been largely on iron catalysts and processes that employ iron. The present bulletin completes the account of studies of cobalt catalysts begun in the previous technical paper [5] and describes the investigation of iron catalysts through 1953.

The reader is referred to references 6 to 15 for publications of the Bureau of Mines between 1948 and 1957 for detailed summaries and bibliographies on the Fischer-Tropsch synthesis; they include accounts of information available in technical literature and in captured German documents, as well as descriptions of Bureau of Mines research.

ACKNOWLEDGMENT

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⁶ Storch, H. H., Fischer-Tropsch and Related Processes for Synthesis of Hydrocarbons by Hydrogenation of Carbon Monoxide: Advances in Catalysis, vol. I, 1948, Academic Press, Inc., New York, N. Y., pp. 115–156; A Review of the Development of Processes for Synthesis of Liquid Fuels by Hydrogenation of Carbon Monoxide: Chem. Eng. Prog., vol. 44, 1948, pp. 469–480.
⁷ Golumbic, N., Anderson, H. C., and Grass, R. C., Revised Bibliography of Bureau of Mines Investigations on the Production of Liquid Fuels From Oil Shale, Coal, Lignite, and Natural Gas (to 1949): Bureau of Mines Inf. Circ. 7534, 1949, 53 pp.
⁸ Storch, H. H., Golumbic, N., and Anderson, R. B., The Fischer-Tropsch and Related Syntheses: John Wiley & Sons, New York, N. Y., 1951, 610 pp.
⁹ Anderson, R. B., Iron Nitrides as Fischer-Tropsch Catalysts: Advances in Catalysis, vol. V, Academic Press, Inc., New York, N. Y., 1953, pp. 355–384. Thermodynamics of the Hydrogenation of Carbon Monoxide and Related Reactions: Catalysis, vol. IV (ed. by P. H. Emmett), Reinhold Publishing Co., New York, N. Y., chap. 1, 1956, pp. 1–28. Catalysts for the Fischer-Tropsch Synthesis: Catalysis, vol. IV (ed. by P. H. Emmett), Reinhold Publishing Co., New York, N. Y., chap. 2, 1956, pp. 29–256. Kinetics and Reaction Mechanism of the Fischer-Tropsch Synthesis: Catalysis, vol.IV (ed.by P. H. Emmett), Reinhold Publishing Co., New York, N. Y., chap. 3, 1956, pp. 257–372.
¹⁰ Anderson, H. C., Wiley, J. L., and Newell, A., Bibliography of the Fischer-Tropsch Synthesis and Related Processes: Part I. Review and Compilation of the Literature on the Production of Synthetic Liquid Fuels and Chemicals by the Hydrogenation of Carbon Monoxide; Part II. Patents: Bureau of Mines Bull. 544, 1954, 965 pp.
¹¹ Hofer, L. J. E., Crystalline Phases and Their Relation to Fischer-Tropsch Catalysts: Catalysis, vol. IV (ed. by P. H. Emmett), Reinhold Publishing Co., New York, N. Y., chap. 4, 1956, pp. 373–442.
¹² Cohn, E. M., The Isosynthesis: Catalysis, vol. IV (ed. by P. H. Emmett), Reinhold Publishing Co., New York, N. Y., chap. 5, 1956, pp. 443–472.
¹³ Greyson, M., Methanation: Catalysis, vol. IV (ed. by P. H. Emmett), Reinhold Publishing Co., New York, N. Y., chap. 6, 1956, pp. 473–508.
¹⁴ Orchin, M., and Wender, I., Reactions of Carbon Monoxide: Catalysis, vol. V (ed. by P. H. Emmett), Reinhold Publishing Co., New York, N. Y., chap. 1, 1957, pp. 1–72.
¹⁵ Benson, H. E., Field, J. H., Bienstock, D., Nagel, R. R., Brumn, L. W., Hawk, C. O., Crowell, J. H., and Storch, H. H., Development of the Fischer-Tropsch Oil-Recycle Process: Bureau of Mines Bull. 568, 1957, 72 pp.

J. T. McCartney, W. H. Tarn, M. Abelson, A. P. Dudash, W. E. O'Neill, Leonard Shaw, R. E. Kelly, C. W. DeLeuze, W. C. Peebles, E. H. Bean, J. J. Curoe, A. M. Whitehouse, H. E. Benson, E. C. Ralston, and George Wilson. We are especially indebted to H. H. Storch, who supervised most of this work, for valuable guidance and inspiration.

PREPARATION AND PROPERTIES OF CATALYSTS

Despite significant advances in theory and the development of refined tools for examining catalysts in the last 20 years, the development of successful catalysts is still largely an empirical art, involving preparation and testing of a large number of samples. However, at present the research worker is guided by a vast store of information regarding the properties of these materials and by a voluminous literature on catalysts and catalytic reactions. For success in a catalyst-development program, the worker should have as complete an understanding of the catalytic system as possible, its composition, the phases present, the pore geometry, and changes of composition and structure during pretreatment and use of the catalyst. Detailed knowledge of the catalytic reaction itself, as well as its mechanism and kinetics, is also required for a rational approach to catalyst development. The first major section of this bulletin will consider methods for preparing catalysts and the results of studies made to elucidate catalyst structure. The second major section will describe tests of catalysts in the Fischer-Tropsch synthesis and the kinetics of the process. The selectivity and mechanism of the process are considered in the third major section.

COBALT CATALYSTS

The preparation and use of cobalt catalysts in the Fischer-Tropsch synthesis have been described previously.[16] Studies of cobalt catalysts were made early in the present research program to determine the structure of catalysts and to elucidate the kinetics and mechanism of the synthesis. At present cobalt Fischer-Tropsch catalysts are not of commercial interest in the United States.

PHYSICAL PROPERTIES

UNREDUCED CATALYSTS

The physical properties of unreduced, precipitated cobalt catalysts which have been studied [17] [18] include surface areas (A) determined by adsorption of nitrogen at $-195°$ C., densities obtained by displacement of helium

and mercury, pore volumes (V), and average pore diameters computed for cylindrical pores $\left(d=\dfrac{4V}{A}\right)$. The pore volume is the volume of pores penetrated by helium but not by mercury at atmospheric pressure—that is, pores with diameters smaller than about 5 microns. Surface areas and pore volumes of unreduced catalysts, Bureau of Mines number 89 (100Co : 6ThO$_2$: 12MgO : 200 kieselguhr), of unreduced catalysts of this type in which one or more of the components have been omitted, and of unreduced Bureau of Mines catalysts 108 (100Co : 18ThO$_2$: 100 kieselguhr) are given in table 1.

The preparations of catalyst 89 were usually reproducible with respect to surface area. All of these catalysts, except 89EE and 89CC, were prepared in small batches (200 to 300 grams). Catalysts prepared with untreated kieselguhrs had higher surface areas than those containing calcined or flux-calcined kieselguhr. The difference was larger than would be expected if the areas of the kieselguhr and of the cobalt-basic carbonate-promoter complex (called "cobalt complex") are assumed to be additive. This effect may result from stabilization of the catalyst structure (on precipitation) by the fine structure of the untreated kieselguhr, or by the formation of cobalt hydrosilicate bonds.

The 89-type catalysts prepared in large batches contained smaller amounts of carbon dioxide (as cobalt basic carbonate) than small batches and were characterized by much higher surface areas, possibly because of differences in precipitating, washing, or drying methods. The surface areas of 108-type catalysts, all of which were prepared in large batches (30 pounds), varied more widely than those of the 89-type catalysts.

On pelleting, the surface areas decreased 10 to 15 percent. Such treatment can compress some of the cobalt-complex particles so that nitrogen molecules cannot penetrate the space between them. A comparison of pelleted catalyst 108B with and without graphite showed that graphite (used as a die lubricant) did not appreciably block the openings of the pores. The mercury and bulk densities of the catalysts increased by a factor of 2 to 3 after pelleting, while the average pore diameter decreased from 500–700 A. to 130–280 A.

[16] Work cited in footnote 5, p. 3.
[17] Craxford, S. R., and Rideal, E. K., Mechanism of the Synthesis of Hydrocarbons From Water Gas: Jour. Chem. Soc., 1939, pp. 1604–1614.
[18] Anderson, R. B., Hall, W. K., Hewlett, H., and Seligman, B., Studies of the Fischer-Tropsch Synthesis. II. Properties of Unreduced Cobalt Catalysts: Jour. Am. Chem. Soc., vol. 69, 1947, pp. 3114–3119.

TABLE 1.—*Properties of unreduced Co-ThO₂-MgO-kieselguhr and Co-ThO₂-kieselguhr catalysts*

Catalyst No.	Form [1]	Co, per-cent	KG, type [2]	Surface area, m.²/gm.			Density, gm./cc.		Pore volume, cc./gm. [4]	Average pore diameter, A. [5]
				KG	Catalyst	Complex [3]	Hg	He		
89-type catalysts (100Co:6ThO₂:12MgO:200 kieselguhr)										
89B	P	----	HSC	1.9	60.4	118.8	----	----	----	----
89H	P	23.9	HSC	1.9	67.2	132.5	1.20	2.74	0.47	280
89I	G	----	HSC	1.9	83.6	165.2	.51	----	1.60	766
89I	P	23.7	HSC	1.9	75.2	148.5	1.27	----	.43	229
89J	G	----	FC	22.2	104.1	186.0	.43	2.87	1.98	760
89J	P	24.5	FC	22.2	88.7	155.2	.97	2.76	.66	297
89K	G	----	Port	17.5	101.1	185.0	.61	2.77	1.28	506
89K	P	24.6	Port	17.5	88.8	160.1	1.20	2.77	.47	212
89L	P	----	HSC	1.9	58.6	115.2	1.34	----	.38	259
89N	P	24.8	HSC⁶	1.9	60.4	118.8	----	----	----	----
89O	G	----	FC⁷	20.8	143.5	266.2	----	----	----	----
89O	P	24.3	FC⁷	20.8	129.2	237.8	.95	----	.69	213
89Q	P	23.8	Port	17.5	85.7	156.0	1.10	----	.55	257
89U	G	----	German	14.9	109.3	203.9	.45	----	1.89	692
89U	P	----	German	14.9	86.2	157.5	1.10	2.80	.55	255
89V	G	----	D-911	29.3	101.9	174.5	.54	2.82	1.50	589
89V	P	----	D-911	29.3	77.6	125.9	1.31	----	.40	206
89Y	P	----	SA5	37.3	72.2	118.0	1.51	----	.30	165
89Z	P	----	658T	25.2	94.6	164.0	1.29	3.08	.41	173
89AA	P	----	JMII	5.5	61.7	118.0	1.48	----	.32	207
89BB	P	----	JMII	5.5	66.2	125.0	1.30	2.86	.40	----
89CC	P	----	FC	22.2	149.6	----	----	----	----	----
89DD	P	----	SF	19.1	93.2	169.2	----	----	----	----
89EE	G	----	FC	22.2	161.1	300.0	.42	2.87	2.04	502
89EE	P	----	FC	22.2	141.5	260.8	1.10	2.80	.45	127
112A⁸	P	----	FC	22.2	78.0	133.8	----	----	----	----
108-type catalysts (100Co:18ThO₂:100 kieselguhr)										
108B	G	----	FC	22.2	84.1	115.4	0.48	----	1.56	742
108B	P	34.0	FC	22.2	71.6	96.6	1.13	3.08	.56	313
108B	LP	----	FC	22.2	66.5	89.0	1.51	----	.34	205
108B⁹	P	----	FC	22.2	77.2	105.0	----	----	----	----
108G	VLP	----	FC	22.2	72.0	97.0	1.30	3.27	.46	257
108H	P	----	FC	22.2	125.0	170.0	----	----	----	----
108I	P	----	FC	22.2	110.5	154.8	----	----	----	----
Special catalysts										
100Co:6ThO₂:12MgO					149.0	149.0	0.68	3.80	1.22	327
100Co:6ThO₂:12MgO					154.8	154.8	.78	3.62	1.00	259
100Co:6ThO₂					171.0	171.0	----	----	----	----
100Co:12MgO					142.6	142.6	----	----	----	----
100Co:8MgO⁹					129.6	129.6	----	----	----	----
100Co:200 HSC KG				1.9	77.2	152.4	----	----	----	----
100Co:200 FC KG				22.2	75.6	124.7	.46	2.71	1.75	926
Co basic carbonate					126.2	126.2	.93	3.81	.82	293

[1] G=granules, broken filter cake; P=pellets, ¼₆ inch long and ⅛ inch in diameter; LP=pellets ¼ inch long and ⅛ inch in diameter; VLP= pellets, ³⁄₁₆ inch long and ⅛ inch in diameter.

[2] Johns Manville kieselguhrs: HSC=Hyflo Super-Cel (flux calcined), JMII (calcined), FC=Filter-Cel (natural), SF=Snowfloss (natural); Dicalite kieselguhrs: D-911 (natural), SA5 (natural), 658T (natural); Port.=Portuguese.

[3] Area of cobalt basic carbonate-promoter complex computed on an additive basis per gram of complex.

[4] Reciprocal of the mercury density minus the reciprocal of the helium density.

[5] Computed by d=4×pore volume/surface area.

[6] Acid-extracted; area probably unchanged.

[7] Acid-extracted.

[8] Contains MgO precipitated during preparation.

[9] Without graphite.

Hysteresis of the adsorption isotherms in the relative pressure region of 0.4 to 0.7 indicated the presence of pores less than 100 A. in diameter.

Mercury did not penetrate the granular or pelleted catalyst, showing that external pores were less than 5 microns in diameter. For granular catalysts the specific volume in mercury (reciprocal of the mercury density) approximated the sum of the specific volume in mercury of the cobalt complex plus that of the kieselguhr; hence, the cobalt complex was deposited only in those pores of the kieselguhr that were larger than 5 microns in diameter. When the catalyst was pelleted, considerable deformation of the kieselguhr structure occurred. The specific volume of the pelleted catalyst in mercury was smaller than that of the kieselguhr it contained.

In the absence of kieselguhr, the surface areas were comparable with those of the cobalt complex of catalysts containing calcined or flux-calcined kieselguhr. Catalysts with neither promoters nor kieselguhr had smaller areas. The addition of precipitated magnesia produced catalysts with lower areas than preparations containing powdered magnesia, either with or without kieselguhr.

Raw catalysts of Bureau of Mines series 108 and 89 were almost completely amorphous to X-rays. The original noncalcined kieselguhrs were also almost entirely amorphous to X-rays, except for Johns-Manville Filter Cel, which showed a weak line corresponding to a Bragg spacing of 3.35 A. The calcined kieselguhrs generally gave the diffraction pattern of cristobalite. A sample of thoria, precipitated in the same manner as catalyst 89K, was completely amorphous. After these catalysts were heated in air for 3 hours at 450° C., they exhibited the diffraction pattern of cobalt oxide CO_3O_4 (isomorph of magnetite), but thoria and kieselguhr produced only a heavy background on the film. A similar heat treatment of kieselguhrs and thoria left them amorphous.

REDUCED CATALYSTS

STRUCTURE

X-ray diffraction was used to determine the structure of cobalt in reduced catalysts. A cobalt-thoria-kieselguhr catalyst (Bureau of Mines 108B) reduced at 350° to 450° C. had an unusual X-ray powder-diffraction pattern of only three lines (table 2). These lines can be indexed as the 111, 220, and 311 lines of face-centered cubic (f. c. c.) β-cobalt, assuming that the 200 and 222 lines do not appear in the pattern. The same lines can also be indexed as the 002, 110, and 112 lines of hexagonal close-packed (h. c. p.) α-cobalt, as-

TABLE 2.—X-ray diffraction data for face-centered cubic, disordered, and hexagonal close-packed cobalt

Face-centered cubic			Disordered	Hexagonal close-packed		
I/I₁[1]	hkl[2]	d/n[3]	d/n[3][4]	d/n[3]	hkl[2]	I/I₁[1]
S	(111)	2.0467	2.0409	2.1645	(100)	W
				2.0234	(002)	M
vW	(200)	1.7725		1.9104	(101)	vS
M	(220)	1.2533	1.2554	1.2522	(110)	S
				1.1494	(103)	S
				1.0831	(200)	W
S	(311)	1.0688	1.0647	1.0655	(112)	S
				1.0469	(201)	M
vW	(222)	1.0233				
				1.0149	(004)	W

[1] Relative intensities: S=strong, M=medium, W=weak, v=very.
[2] Miller indices.
[3] Interplanar spacings in A.
[4] Obtained with a reduced catalyst (Bureau of Mines 108B).

suming that the 100, 101, 103, and 201 lines do not appear. From data published by Edwards and Lipson [19] and Wilson [20] and from the fact that the diffraction patterns revealed very faint traces of the 100 and 101 h. c. p. and the 200 f. c. c. reflections, it was deduced that the cobalt-thoria-kieselguhr catalyst had a highly disordered layer structure after reduction. If the h. c. p. structure is visualized as successive, close-packed layers of atoms placed one upon the other so that the corresponding atoms in every second layer are directly above each other, the sequence of layers may be represented by ABABAB ---. The f. c. c. structure may be visualized as successive, close-packed layers of atoms such that the corresponding atoms of every third layer are placed directly above each other. The sequence of layers is then ABCABCABC----. This configuration was proposed by Edwards and Lipson,[21] who also postulated that an h. c. p. structure may exist in which the sequence of layers is not invariably ABABAB---, but in which a fault occasionally occurs to yield, for example, ABABABABCBCBCBC-ACACA---. The diffraction pattern of such a structure would correspond to those observed. This fault-filled, hybrid structure with a maximum disorder was obtained by reduction of the catalyst at or below the α–β transition temperature (about 400° C.). The lattice parameter of the disordered cobalt, as determined by a modification of the method of Davey,[22] was 3.539±0.003A, in excellent agreement with the value (3.545±0.005 A.) given in the review

[19] Edwards, O. S., and Lipson, H., Imperfections in the Structure of Cobalt. I. Experimental Work and Proposed Structure: Proc. Roy. Soc. (London), ser. A, vol. 180, 1942, pp. 268–277.
[20] Wilson, A. J. C., Imperfections in the Structure of Cobalt. II. Mathematical Treatment of Proposed Structure: Proc. Roy. Soc. (London), vol. 180, 1942, pp. 277–285.
[21] Work cited in footnote 19 above.
[22] Davey, W. P., A Study of Crystal Structure and Its Applications: McGraw Hill Book Co., Inc., New York, N. Y., 1934, p. 163.

of Neuburger.[23] [24] X-ray diffraction patterns of partly reduced catalysts failed to show any lines; this was undoubtedly due to obscuring of reflections by the background.

SURFACE AREA AND PORE VOLUME

For convenience, changes that occur during reduction of precipitated cobalt oxides or carbonates may be divided into three classes: Sintering, shrinkage, and reorientation of the reduced cobalt. Most reduction processes are believed to occur at the interface between metal and metal oxide, and in some systems the rate of formation of nuclei of metal largely determines the kinetics of reduction. If metal and oxide do not form a solid solution, a slow rate of nuclei formation will result in an autocatalytic reduction process, the rate increasing with time in the early stages.[25] The presence of a small fraction of an oxide A that is more easily reduced than oxide B will usually increase the rate of reduction of oxide B, possibly by the formation of a large number of nuclei of metal A early in the reduction. Conversely, small fractions of an oxide C that is less easily reduced than oxide B usually decrease the rate of reduction of oxide B.

The presence of oxides of type C usually produces and maintains reduced metal of higher surface area than obtained from B alone, and the presence of type A leads to structures of lower area. If considerable reorientation of the freshly reduced metal does not occur, the decrease in volume during reduction should make the metal-to-oxide interface accessible to the reducing gas.

German work on the development of cobalt catalysts demonstrated that the presence of copper permitted a decrease of reduction temperature from 350° to 200° C.; however, these catalysts had very short lives, and copper-promoted preparations were abandoned early in their development program. On this basis the Bureau of Mines investigated only the functions of the desirable additives—thoria, magnesia, and kieselghur—on the structure of cobalt catalysts.

Reduced cobalt-thoria-magnesia-kieselguhr and cobalt-thoria-kieselguhr catalysts and similar preparations with one or more of the components omitted have been investigated [26] by measurement of surface area and chemisorption of carbon monoxide at −195° C. and by determinations of mercury and helium densities. These studies showed that the presence of

thoria and magnesia decreases the rate of reduction and prevents excessive sintering; that an appreciable fraction of the surface is occupied by promoter; and that kieselguhr as a carrier is moderately effective in preventing the decrease in surface area on reduction but that its most important function is to prevent the decrease in bulk volume of the catalyst on reduction. In reduction, the area of cobalt-promoter complex of cobalt-thoria-magnesia–kieselguhr catalysts decreased to about 60 percent of its area in the raw state, while for cobalt-thoria-kieselguhr catalysts the area decreased to 40 percent of its original value. Of the promoters, magnesia was more effective in retarding sintering than thoria. Kieselguhr was about as effective in retarding sintering as the thoria. The natural kieselguhr (F. C.) was more effective than the flux-calcined support (H. S. C.). Data in table 3 indicate that the surface-area changes are the result of (a) thermal decomposition of cobalt basic carbonate while the catalyst was heated to reduction temperature in nitrogen, and (b) reduction of the cobalt oxide or basic carbonate to metal. For the cobalt-thoria-magnesia preparation, both with and without kieselguhr, the largest surface area diminution occurred in step (a). For preparations without promoters, a large degree of sintering occurred in both steps, the preparation supported on kieselguhr being more resistant to sintering.

Although kieselguhr is somewhat effective in preventing excessive diminution of surface area during reduction, its principal function is to prevent excessive shrinkage of the particle, as shown by mercury density data in table 4. Although mercury wetted and penetrated the particles of reduced cobalt basic carbonate, mercury did not wet or penetrate the particles of the samples containing either promoters or kieselguhr. On reduction, the volume of mercury displaced per gram of catalyst (in the unreduced state) decreased by less than 5 percent for samples containing kieselguhr, whether or not the catalyst contained promoters and whether the samples were in the form of granules or pellets. The volume of mercury displaced by the unsupported catalyst decreased, on reduction, to less than half of the initial volume. The pore volumes (table 4) of all preparations containing kieselguhr increased on reduction; however, those of unsupported samples decreased. Average pore diameters computed from the equation of Emmett and DeWitt [27] ($d=4 \times$ pore volume/surface area) increased on reduction, because the decrease

[23] Neuburger, M. C., [Lattice Constants for 1936]: Ztschr. Kristal., vol. 93, 1936, pp. 1–36.

[24] Titles in brackets are translations from the language in which the reference cited was originally published.

[25] Langmuir, I., Constitution and Fundamental Properties of Solids and Liquids. I. Solids: Jour. Am. Chem. Soc., vol. 38, 1916, pp. 2221–2295.

[26] Anderson, R. B., Hall, W. K., and Hofer, L. J. E., Studies of the Fischer-Tropsch Synthesis, IV. Properties of Reduced-Cobalt Catalysts: Jour. Am. Chem. Soc., vol. 70, 1948, pp. 2465–2472.

[27] Emmett, P. H., and DeWitt, T. W., The Low-Temperature Adsorption of Nitrogen, Oxygen, Argon, Hydrogen, n-Butane, and Carbon Dioxide on Porous Glass and on Partially Dehydrated-Chabazite: Jour. Am. Chem. Soc., vol. 65, 1943, pp. 1253–1262.

TABLE 3.—*Changes in surface area during heating and reduction*

All data per gram of original unreduced catalyst or complex

Catalyst	Original Area, m.²/gm.	Original Area of complex per gram complex	Heated[1] Area, m.²/gm.	Heated[1] Area of complex per gram complex	Evacuated[1] Area, m.²/gm.	Evacuated[1] Area of complex per gram complex	Reduced[1] Area, m.²/gm.	Reduced[1] Area of complex per gram complex
100Co : 6ThO₂ :12MgO : 200 kieselguhr, 89J	85. 5	155. 4	65. 5	108. 9	67. 0	109. 8	62. 0	99. 6
100Co:6 ThO₂:12MgO	154. 8	154. 8	68. 3	68. 3	61. 1	61. 1	52. 8	52. 8
100Co:200 kieselguhr[2]	75. 6	124. 7	37. 1	52. 4	35. 5	49. 2	18. 3	14. 2
Cobalt basic carbonate	126. 2	126. 2	24. 2	24. 2	21. 6	2. 5	2. 5	2. 5

[1] Area of catalyst and complex per gram of catalyst and per gram of complex in the original unreduced catalyst, respectively.   [2] Contains Filter-Cel.

TABLE 4.—*Mercury and helium densities of unreduced and reduced cobalt catalysts*

Catalyst	Form[1]	Unreduced Densities gm./cc. Hg	Unreduced Densities gm./cc. He	Unreduced Pore volume, cc./gm.	Unreduced Area, m.²/gm.	Unreduced $\bar{d}^2$, A.	Reduced Densities gm./cc. Hg	Reduced Densities gm./cc. He[3]	Reduced Pore volume, cc./gm.[4]	Reduced Area, m.²/gm.[4]	Reduced $\bar{d}^2$, A.	Mercury volumes before reduction	Mercury volumes after reduction
100Co : 6ThO₂ : 12 MgO : 200 kieselguhr													
89-H	P	1. 20	2. 74	0. 47	67. 2	280	0. 993	3. 10	0. 68	51. 8	527	0. 833	0. 816
89-J	P	. 974	2. 76	. 66	88. 7	297	. 780	3. 07	. 95	76. 6	500	1. 026	1. 037
89-K	P	1. 20	2. 77	. 47	88. 8	212	1. 045	3. 08	. 63	77. 4	327	. 833	. 768
89-K	G	. 611	2. 77	1. 28	101. 1	506	. 537	3. 13	1. 54	76. 8	804	1. 635	1. 530
89-U	P	1. 10	2. 80	. 55	86. 2	255	. 901	3. 08	. 79	46. 7	672	. 909	. 896
89-FF	P	1. 295	(5)	. 41	102. 9	160	1. 138	3. 03	. 55	99. 0	222	. 772	. 712
100Co : 18ThO₂ : 100 kieselguhr													
108-B	P	1. 13	3. 08	0. 56	71. 6	313	0. 905	3. 69	0. 73	42. 3	693	0. 885	0. 836
Special catalysts													
100Co:6ThO₂: 12MgO 100Co:200	G	0. 781	3. 62	1. 00	154. 8	259	1. 057	6. 72	0. 80	84. 1	379	1. 280	0. 593
kieselguhr	G	. 457	2. 71	1. 75	75. 6	926	. 378	3. 00	2. 31	22. 8	4,060	2. 189	2. 082
Cobalt basic carbonate	G	. 925	3. 81	. 82	126. 1	293	[6]4. 476	9. 00	. 112	4. 2	1,070	1. 081	. 125

[1] P=pellets (1.6 mm. long by 3.2 mm. diameter); G=granules, broken filter cake.
[2] Average pore diameters computed from $\bar{d}=4V/A$, where V is the pore volume and A the surface area per gram.
[3] Helium densities calculated from compositions of reduced catalysts: 89-type, 3.12; 108B, 3.69; Co:ThO₂:MgO=100:6:12, 7.79; Co:kieselguhr=100:200, 3.06: and cobalt basic carbonate, 8.9.
[4] Pore volumes and surface areas per gram of reduced catalyst.
[5] Not determined; assumed to be 2.77.
[6] This sample wet by mercury.

in surface area was always of a greater magnitude than the changes in pore volume.

At −195° C. carbon monoxide seems to be chemisorbed only on the metallic cobalt in the catalyst surface. Actually, the isotherm at this temperature is a composite of chemical and physical adsorption; the volume of chemisorbed carbon monoxide is obtained by subtracting the adsorption isotherm of nitrogen from the total carbon monoxide isotherm, both isotherms being

TABLE 5.—*Chemisorption of carbon monoxide on reduced cobalt Fischer-Tropsch catalysts*

All data per gram of unreduced catalyst

Catalyst	Form [1]	V_m, cc.	V_{CO}, cc.[2]	Absorption by complex per gram of complex, cc.		$\dfrac{V_{CO}}{V_m \text{ of complex}}$	Co atoms in surface, percent [3]
				V_m	V_{CO}		
100Co:6ThO₂:12MgO:200 kieselguhr							
89H	P	9. 58	4. 40	18. 72	8. 80	0. 470	72. 3
89J	P	14. 15	3. 10	23. 92	6. 20	. 259	39. 9
89K	P	14. 31	3. 80	24. 80	7. 60	. 306	47. 1
89K	G	14. 19	4. 00	24. 40	8. 00	. 328	50. 4
89U	P	8. 64	2. 17	13. 98	4. 34	. 311	47. 9
100Co:18ThO₂:100 kieselguhr							
108B	P	7. 40	2. 56	11. 42	2. 84	0. 448	69. 0
Special catalysts							
100Co:6ThO₂:12MgO	G	12. 06	6. 90	12. 06	6. 90	0. 572	88. 0
100Co:6ThO₂	G	3. 33	1. 95	3. 33	1. 95	. 586	90. 2
100Co:12MgO	G	8. 03	3. 70	8. 03	3. 70	. 461	71. 0
100Co:200 KG [4]	G	4. 18	. 85	3. 28	1. 70	. 518	79. 7
Cobalt basic carbonate	G	. 58	. 36	. 58	. 36	. 632	97. 2
Cobalt oxide powder		. 73	. 73	. 48	. 48	. 648	99. 7

[1] G=granules, broken filter cake; P=pellets.
[2] Vco computed from the difference of the total carbon monoxide sotherms and the physically adsorbed nitrogen at equal relative pressures.

[3] Vco/V_m=complex divided by 0.65, the value of Vco/V_m=complex for cobalt metal.
[4] Filter-cel.

plotted on a relative pressure basis. This approximation is permissible, since the physical properties of the two molecules, including molecular size, are nearly identical. For the samples without kieselguhr or promoters, which in the reduced state were essentially pure cobalt, the ratio of chemisorbed carbon monoxide (V_{co}) to the nitrogen monolayer (V_m) was about 0.65 (table 5). Possibly this ratio arises from the steric factors involved in chemisorption on fixed sites. For all promoted and/or supported catalysts, the ratio of V_{co} to V_m for the complex was lower than 0.65. The lowest values of this ratio were obtained for promoted and supported catalysts, and for these samples it may be inferred that more than 30 percent of the surface of the complex contained material other than metallic cobalt.

Structural changes during reduction of a number of metal oxides and catalysts were determined by electron microscopy and surface-area measurements.[28][29] Cobaltous oxide was prepared from the nitrate by precipitation with aqueous ammonia;[30] the preparation of cobalt-

thoria-magnesia-kieselguhr catalyst and combinations of cobalt and promoters or carrier by precipitation with sodium carbonate solution has already been described.[31][32] A number of other metal oxides was prepared by the addition (with vigorous stirring) of an equivalent amount of sodium hydroxide solution to boiling solutions of silver, cupric, nickelous, or ferric nitrates. The samples were dried at 100° C. before use, placed in a special adsorption tube with a four-way stopcock,[33] evacuated for 1 hour at 100° C., and reduced in an automatically controlled resistance furnace. The weight loss on reduction and the surface area after reduction were determined. The reduced samples were then transferred in a stream of carbon dioxide to a tube filled with benzene, and samples wet with benzene were used for the electron-microscope studies to avoid atmospheric oxidation. For examination by the electron microscope, the large, coherent aggregates obtained in some precipitates were gently crushed in a mortar in an attempt to separate the material into its basic crystallites (see p. 136).

[28] McCartney, J. T., and Anderson, R. B., Crystalline Aggregation of Cobalt Powder: Jour. Appl. Phys., vol. 18, 1947, pp. 902–903.
[29] McCartney, J. T., Seligman, B., Hall, W. K., and Anderson, R. B., An Electron-Microscopic Study of Metal Oxides and Metal Oxide Catalysts: Jour. Phys. Colloid Chem., vol. 54, 1950, pp. 505–519.
[30] Hofer, L. J. E., and Peebles, W. C., Preparation and X-Ray Diffraction Studies of a New Cobalt Carbide: Jour. Am. Chem. Soc., vol. 69, 1947, pp. 893–899.

[31] Work cited in footnote 18, p. 4.
[32] Anderson, R. B., Krieg, A., Seligman, B., and O'Neill, W. E., The Fischer-Tropsch Synthesis. I. Tests of Cobalt Catalysts at Atmospheric Pressure: Ind. Eng. Chem., vol. 39, 1947, pp. 1540–1554.
[33] Anderson, R. B., Improved Adsorption Vessel: Ind. Eng. Chem., Anal. Ed., vol. 18, 1946, p. 156.
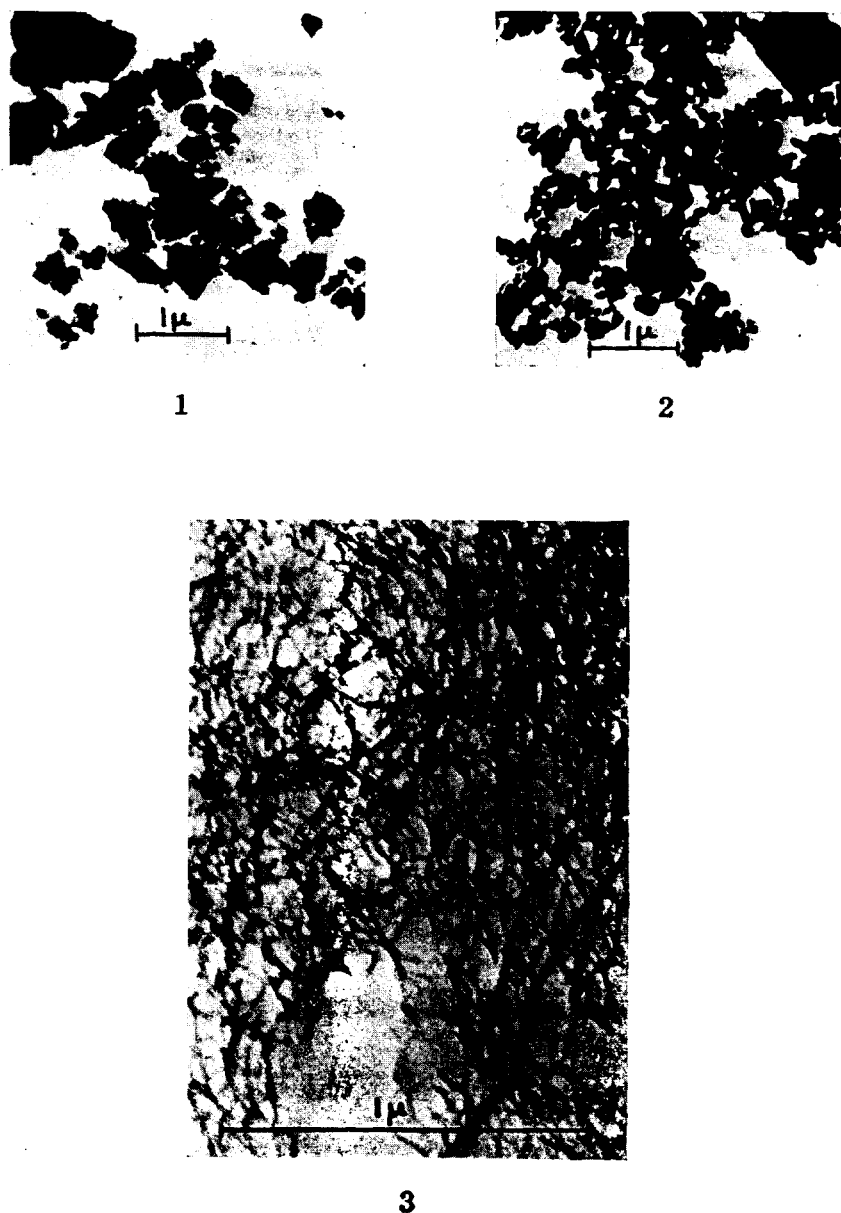
1

2

3

FIGURE 1.—Electron Micrographs of Precipitated Ferric Oxide:

1, Ferric oxide gel; *2*, reduced ferric oxide gel; *3*, ferric oxide sol.

Surface-area changes during reduction are summarized in table 6 for various metal oxides and catalysts; the reduction conditions are also shown. Figures 1 to 5 (micrographs *1* to *19*) show electron micrographs of these oxides and catalysts. Table 6 compares the values for the average particle size and the surface area obtained from these micrographs with the corresponding values obtained from adsorption measurements.

The micrograph of cobalt basic carbonate (No. *12*, fig. 4) shows a large fraction of fine particles. Hydrous oxides of iron (No. *1*, fig. 1) and nickel (No. *4*, fig. 2), on the other hand, were composed of relatively large particles, although their high surface areas indicated the existence of a fine structure similar to that of cobalt basic carbonate. Micrograph *3* (fig. 1), showing a ferric oxide prepared in a more dilute solution than the gel in micrograph *1*, suggests that ferric oxide gels probably have a fibrous structure. Although the cobaltous oxide (No. *10*, fig. 3) was a fine powder, its geometric surface area, estimated from the micrograph, was only 6 percent of the adsorption area; conversely, the oxides of copper (No. *6*, fig. 2) and silver (No. *8*, fig. 3) appeared to have very little internal surface or porosity.
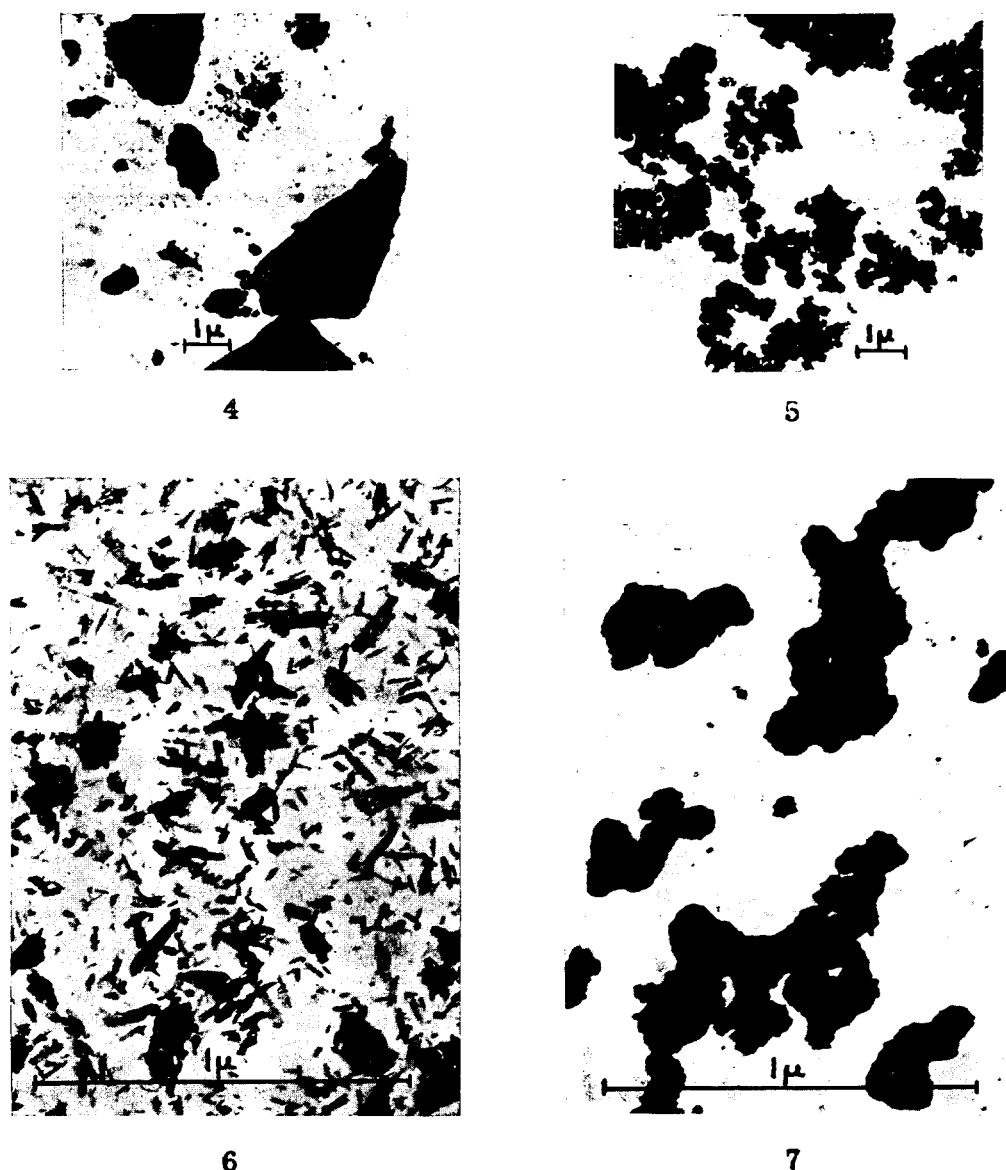
4

5

6

7

FIGURE 2.—Electron Micrographs of Precipitated Nickel and Copper Oxides:

4, Hydrous nickel oxide; *5*, same, reduced; *6*, copper oxide; *7*, same, reduced.

Upon reduction, the surface areas of these samples decreased from 5- to 50-fold, and the existence of relatively less internal surface was indicated. In the reduction of cobaltous oxide (precipitated with ammonia) (fig. 3, nos. *11a, b, c*), the original irregular particles were sintered into larger, smooth particles of cobalt metal, more or less closely aggregated into hexagonal platelets, with diameters ranging from 7 to 25 microns. The hexagons, which were also discernible with the optical microscope, may have been formed by forces similar to those operating in normal crystal formation. However, as the component particles did not entirely lose their identity and the aggregates were easily fractured, they can hardly be classed as true crystals. Possibly the forces acting to combine atoms into crystals are so small when the combining units are particles of relatively large size that only superficial crystal formation occurs. With cobalt basic carbonate, hexagonal platelets were not formed during reduction at 250° or 400° C., although extensive sintering did occur (fig. 4, Nos. *13* and *14*). In the reduction of the basic carbonate the failure to form hexagonal platelets may be due to differences in the structure of the original material or to the presence of traces of sodium in the basic carbonate.

Micrographs *14* and *15* (fig. 4) and *16* and *17* (fig. 5) show that kieselguhr prevented sintering during reduction, that magnesia and thoria
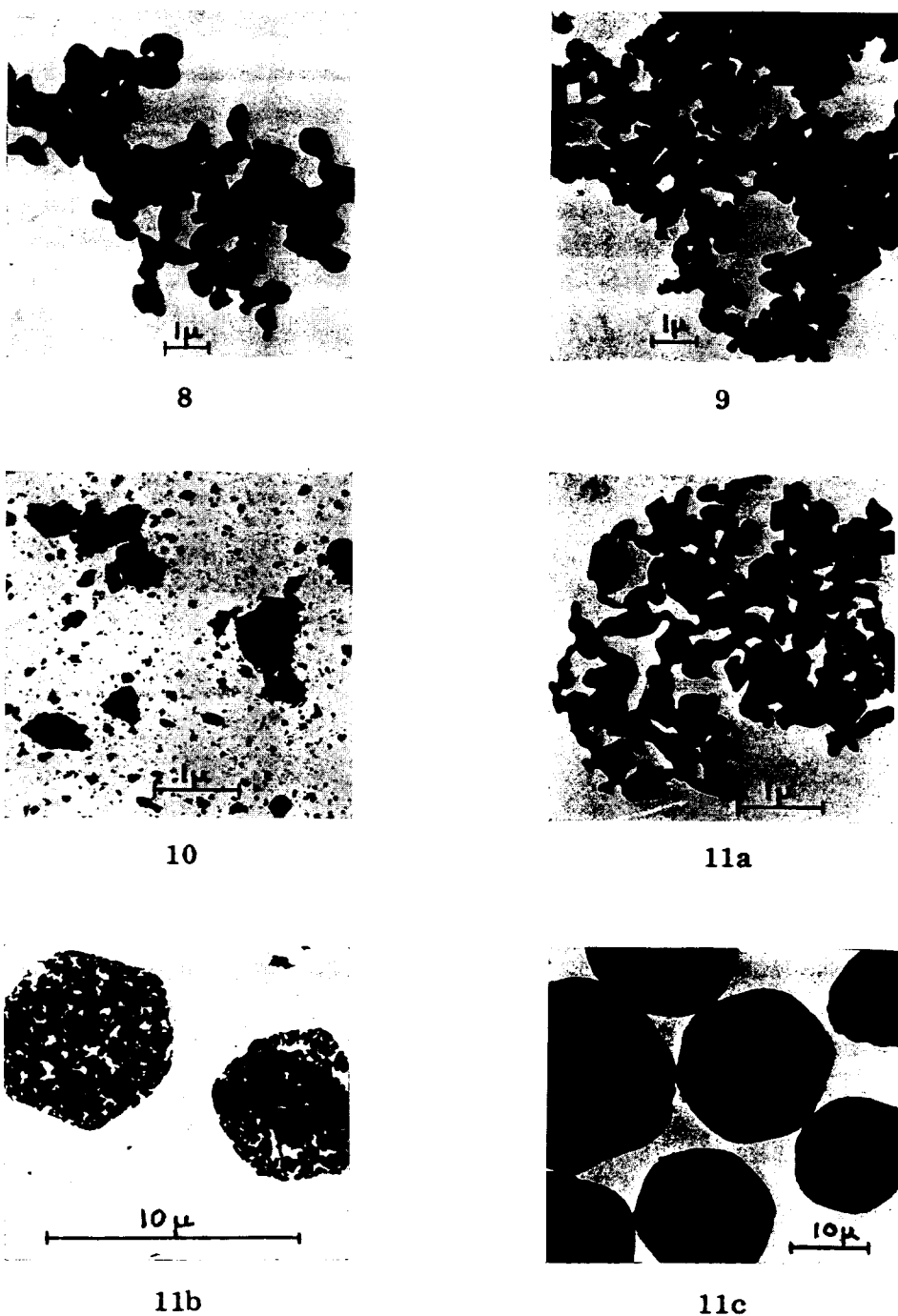
FIGURE 3.—Electron Micrographs of Precipitated Silver Oxide and Cobaltous Oxide:

8, Silver oxide; *9*, same, reduced; *10*, cobaltous oxide; *11*, same, reduced, in various stages of dispersion.

were more effective, and that the combination of both promoters and carrier was most effective in preserving a structure of high surface area. The surface areas of the samples containing promoters were greater than those estimated from average particle diameters, indicating the presence of internal surface area. The promoters probably were intimately mixed with the basic carbonate, and during the reduction a matrix of relatively unchanged promoter remained. The basic carbonate decreased in volume during reduction to the metal, but the isolation of groups of metal atoms in the matrix of the promoter prevented the growth of large crystallites of metal. Kieselguhr may prevent sintering in a similar but less effective manner,