As has been stated, the catalysts other than those belonging to the 10, 47, and 80 series do not form groups sufficiently integrated to permit many conclusions. Catalyst 48A was precipitated with sodium hydroxide, 81A and 81B with sodium carbonate; otherwise, they were similar to the 10 and 80 series. They are inactive and it was suggested in the section on Diffraction Studies that this is related to the use of sodium. Both 48A and 81B have quite high magnetic susceptibility. These experimental facts may be related to the observation of Michel and Chaudron[81] that the solid-solution limit of sodium oxide in γFe_2O_3 is much more readily hydrolyzed than the corresponding solid solution of potassium oxide. Catalyst 50A has a very high magnetic susceptibility, and this is obviously related to the presence of magnetite indicated by the X-ray diffraction pattern. The magnetic studies of the rest of the unpromoted iron catalysts are quite meaningless because of the uncertainty of the catalyst composition.

MAGNETIC AND X-RAY DIFFRACTION STUDIES OF PROMOTED IRON CATALYSTS

Catalysts 1E, 11A, and 5A, prepared from ferric salts with alkali hydroxides, were promoted with cupric nitrate. All these catalysts were very unusual in that the X-ray diffraction pattern (see fig. 40) showed them to be quite amorphous. The magnetic susceptibility of cupric oxide is only 3.8×10^{-6}, and the magnetic susceptibility of hematite is not much greater. The fact that the susceptibility of copper-promoted ferric catalysts 1E and 5A (table 56), which have been subjected to no reducing action, should be 880×10^{-6}, and 290×10^{-6}, respectively, is very surprising and shows that in these catalysts the iron oxide and copper oxide are not simply mixed together. This system CuO–Fe_2O_3 has been studied by Wartmann and Thompson,[82] Forestier and Longuet,[83] and Milligan and Holmes.[84] Interestingly enough, Forestier and Longuet have shown that copper ferrite, a ferromagnetic compound whose crystal structure is closely related to that of spinel and magnetite, can be prepared by adding sodium hydroxide to a mixture of ferric and cupric salts and boiling several hours. Milligan and Holmes have not been able to duplicate these results. The high magnetic susceptibility of 1E, 11A, and 5A (table 56) seems to indicate that there is some incipient formation of ferrite, and the high field dependence of the magnetic susceptibility of 1E supports this contention. On the other hand, our data agree with Milligan and Holmes's results, which show that these catalysts are amorphous as far as X-ray diffraction is concerned. It is interesting to note that the catalyst 5A prepared from ferric chloride has a lower magnetic susceptibility than those prepared from the nitrates.

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[81] Work cited in footnote 79, p. 155.

[82] Wartmann, F. S., and Thompson, A. J., Preparation and Properties of Copper Ferrite: Bureau of Mines Rept. of Investigations 3228, 1934, pp. 15–22.

[83] Forestier, H., and Longuet, J., Chimie physique—formation du ferrite de cuivre à basse temperature: Compt. rend., vol. 208, 1939, pp. 1729–1730.

[84] Milligan, W. O., and Holmes, J., X-Ray Diffraction Studies in the System CuO–Fe_2O_3: Jour. Am. Chem. Soc., vol. 63, 1941, pp. 149–150.

TABLE 56.—*X-ray diffraction patterns and magnetic studies of promoted iron catalysts*

Catalyst No.	Phases	Diffuseness of pattern	Magnetic susceptibility, $\times10^{-6}$
1E		(X)	880
5A		(X)	290
11A		(X)	13,400
23A	See 23B		
23B	Fe_3O_4 (magnetite)	(A)	7,800
24A	See 24B		
24B	Fe_3O_4; $\alpha Fe_2O_3 \cdot H_2O$	(B)	3,800
24C	Fe_3O_4	(A)	15,800
25A	do	(A)	1,860
40A		(X)	100
85A	Fe_3O_4	(A)	18,000

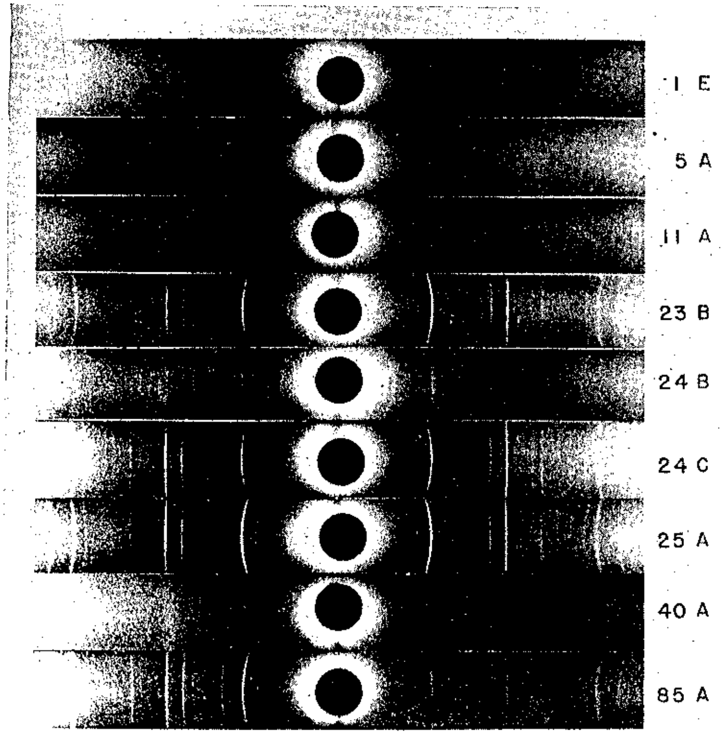

FIGURE 40.—X-ray diffraction patterns of promoted iron catalysts.

Catalysts 23B, 24B, and 25A were prepared by precipitating ferrous sulfate and cupric sulfate with KOH, K_2CO_3, and NaOH, respectively. In every case the diffraction pattern (see fig. 40) revealed the presence of magnetite. The reason the magnetite pattern appeared here seems to be related to the fact that both ferrous and ferric (some ferric iron was probably formed by oxidation of ferrous iron during preparation) iron were present in additon to cupric copper, whereas in 1E, 5A, and

11A only ferric iron and cupric copper were present. As was expected, the presence of magnetite was accompanied by high magnetic susceptibility. Catalyst 85A was prepared from ferrous chloride, cupric chloride, and potassium carbonate. As would be expected, it was very similar to catalysts 23B, 24B, and 25A. Catalyst 40A, prepared from ferric nitrate, zinc nitrate, and potassium carbonate, was completely amorphous to X-rays (see fig. 40). In this respect it was very similar to 1E, 5A, and 11A. Heating the promoted iron catalysts for 2 hours at 250° C. had little significant effect.

SURFACE PROPERTIES OF FISCHER-TROPSCH CATALYSTS

Two factors related to the activity of a catalyst are area and accessibility of the catalyst surface. If the surfaces of catalysts are equally accessible, the activity may be expected to vary directly with the area of the active component present. This may refer to the entire surface of a particular component or to active centers which may comprise only a small fraction of the area of this component. Emmett[85] [86] and Harkins[87] have developed methods for determining surface areas by interpretation of the adsorption isotherms of various gases on the catalysts. The total area may be estimated by selecting a point on the physical adsorption isotherm which corresponds to the number of molecules necessary to cover the surface with a layer 1 molecule thick. The area per adsorbed molecule usually is estimated from the density of the adsorbate in the liquid phase. Physical adsorption of most adsorbates is nonselective and hence gives the total surface area. For some components of the surface, it is possible to find gases that will chemisorb specifically on certain of its components in layers only 1 molecule thick; for example, the chemisorption of hydrogen and carbon monoxide on iron,[88] of carbon monoxide on nickel[89] and cobalt (this work), and carbon dioxide on alkaline oxides.[88] It is possible to determine, in at least some cases, the pore distribution of a catalyst for pores smaller than 0.5 micron in diameter from the shape of the higher relative pressure region of the adsorption isotherm. Further information on pore distribution can be obtained from determinations of specific volumes of catalysts, using mercury and helium as immersing fluids, since at atmospheric pressure mercury will not penetrate cylindrical pores smaller than about 5 microns in diameter. More elaborate experiments, in which the amount of mercury forced into capillaries of the catalyst at various pressures up to 10,000 p. s. i. is measured, will give complete pore-distribution curves.[90] In the next few pages, nitrogen and carbon monoxide isotherms (at −195° C.) of various unreduced and reduced Fischer-Tropsch catalysts are presented, along with their interpretation. These isotherms were determined by the conventional volumetric method,[91] and the total surface areas were determined using the simple Brunauer, Emmett, and Teller equation,[92] [93] with the cross-sectional area of the nitrogen molecule taken as $16.2\text{A}^{\circ 2}$. The mercury densities were determined at a pressure of about 1,000 millimeters of mercury. An apparatus similar to that described by Rossman and Smith[94] was used for the helium density determinations. For the adsorption work and the helium and mercury densities the samples were pumped for 1 hour at 100° C. before the determination.

COBALT FISCHER-TROPSCH CATALYSTS

Cobalt Fischer-Tropsch catalysts, as prepared and tested at the Bureau of Mines, contain in addition to cobalt, kieselguhr (KG) as a carrier, and thoria, and in some cases thoria and magnesia as promoters. The Fischer catalyst contained $\text{Co} : \text{ThO}_2 : \text{KG} = 100 : 18 : 100$, while the Hall catalyst contained $\text{Co} : \text{ThO}_2 : \text{MgO} : \text{KG} = 100 : 6 : 12 : 200$. The kieselguhrs vary with both source and method of preparation. The properties of five kieselguhrs will be described briefly as examples.[95] Surface areas and bulk densities were determined on the samples, and electron micrographs were made by J. T. McCartney on the Bureau of Mines electron microscope. The properties of the various kieselguhrs are given in table 57, with the source of the material, and in figure 41, *a* to *e*, the electron micrographs of these samples are shown at a magnification of 2,100. The surface areas and the bulk densities agree in at least a qualitative manner with the electron micrographs; the areas that may be estimated from the micrographs are of the same order of magnitude as the surface areas obtained by the adsorption method. The more compact structure of the Portuguese kieselguhr accounts for the higher bulk density of this sample. Chemical analyses in table 58 show that iron and aluminum are the chief impurities. Filter-Cel, Hyflo Super-Cel, and Portuguese kieselguhr have about equal amounts of iron, while Dicalite 911 and German kieselguhr have higher iron content, and the German kieselguhr has less aluminum.

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[85] Emmett, P. H., and Brunauer, S., The Use of Low-Temperature van der Waals Adsorption Isotherms in Determining the Surface Area of Iron-Synthetic Ammonia Catalysts: Jour. Am. Chem. Soc., vol. 59, 1937, pp. 1553–1564.

[86] Brunauer, S., Emmett, P. H., and Teller, E., Adsorption of Gases in Multimolecular Layers: Jour. Am. Chem. Soc., vol. 60, 1938, pp. 309–319.

[87] Harkins, W. D., and Jura G., Surfaces of Solids XII, An Absolute Method for the Determination of the Area of a Finely Divided Crystalline Solid. Surfaces of Solids XIII, A Vapor Adsorption Method for the Determination of the Area of a Solid Without the Assumption of a Molecular Area, and the Areas Occupied by Nitrogen and Other Molecules on the Surface of a Solid: Jour. Am. Chem. Soc., vol. 66, 1944, pp. 1362–1373.

[88] Brunauer, S., and Emmett, P. H., Chemisorptions of Gases on Iron Synthetic Ammonia Catalysts: Jour. Am. Chem. Soc., vol. 62, 1940, pp. 1732–1746.

[89] Emmett, P. H., and Skau, N., The Catalytic Hydrogenation of Benzene over Metal Catalysts: Jour. Am. Chem. Soc., vol. 65, 1943, pp. 1029–1035.

[90] Ritter, H. L., and Drake, L. C., Pore-Size Distribution in Porous Materials. Pressure Porosimeter, and Determination of Complete Macropore Size Distributions. II. Macropore Size Distributions in Some Typical Porous Substances: Ind. Eng. Chem., Anal. Ed., vol. 17, 1945, pp. 782–791.

[91] Emmett, P. H., in Kraemer's "Advances in Colloid Science": Interscience Publishers, New York, vol. 1, 1942, p. 1.

[92] Work cited in footnote 86, p. 158.

[93] Work cited in footnote 87, p. 158.

[94] Rossman, R. P., and Smith, W. R., Density of Carbon Blocks by Helium Displacement: Ind. Eng. Chem., vol. 35, 1943, pp. 972–976.

[95] For general discussion on types of kieselguhr see Calvert, Diatomaceous Earth: Chemical Catalog Co. New York, 1930, 251 pp.

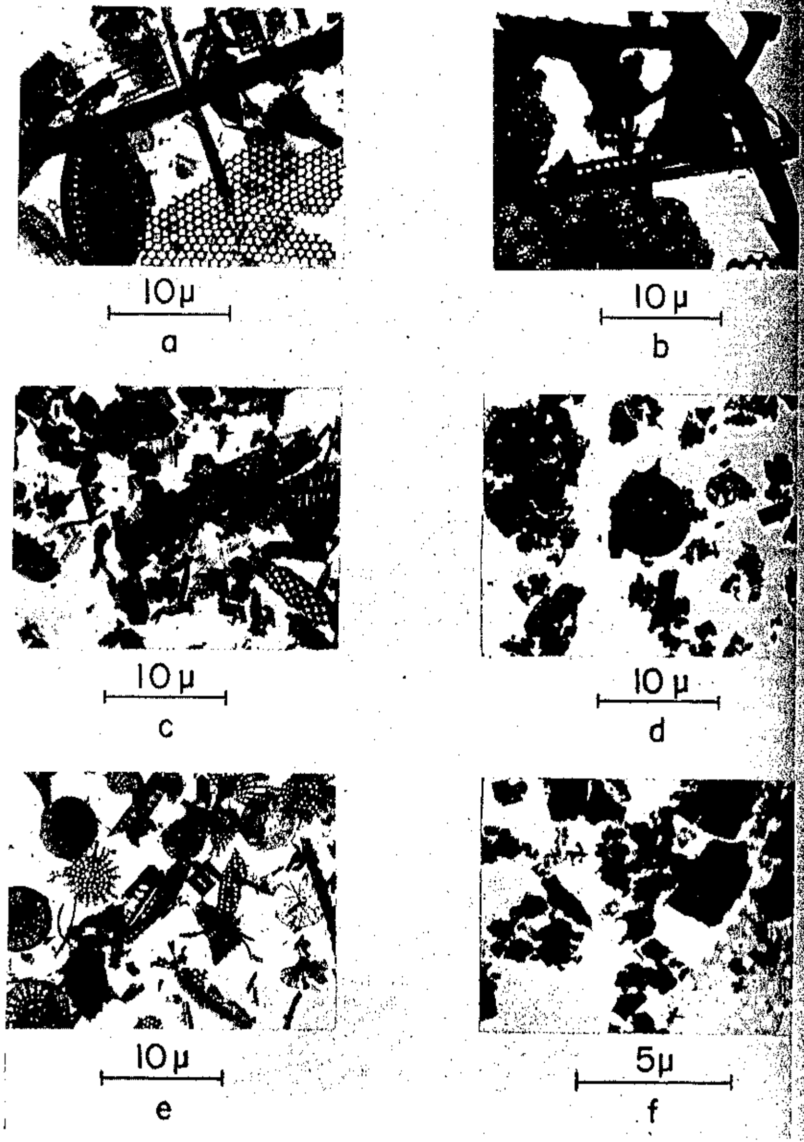

FIGURE 41.—Electron micrographs of kieselguhrs and a Fischer catalyst (made by J. T. McCartney): *a*, Filter-Cel kieselguhr (×2,100); *b*, Hyflo Super-Cel kieselguhr (×2,100); *c*, Dicalite 911 kieselguhr (×2,100); *d*, Portuguese kieselguhr (×2,100); *e*, German kieselguhr (×2,100); *f*, cobalt Fischer catalyst 108–B containing Filter-Cel kieselguhr (×5,400).

TABLE 57.—*Properties of kieselguhrs*

	Bulk density, g./cc.	Surface area, m.²/g.	Pore volumes,[1] cc./g.			Source	Used in 89-catalyst preparations, No.
			Micro.	Macro.	Total		
Filter-Cel (Johns Manville).	0.15	22.2	2.81	3.32	6.13	Marine KG, uncalcined, Lompoc, Calif.	J
Filter-Cel (acid-extracted) (Johns Manville).	---	----	----	----	---	Same as above, but acid-extracted.	O
Hyflo Super-Cel (Johns Manville).	.22	1.9	2.27	1.77	4.04	Same as Filter-Cel, but alkali-treated and sintered at high temperature.	A to I, L, N
Dicalite 911 (Dicalite Co.)	.25	20.3	2.22	1.41	3.63	Fresh water KG from Terrebonne, Oreg.	V
Portugese kieselguhr	.33	17.5	1.47	.93	2.40	Probably a fresh-water KG. This material used by Dr. C. C. Hall of British Fuels Research Board for F. T. catalysts.	K, Q
German kiesselguhr	.14	14.9	3.22	3.62	6.84	From catalyst factory, Ruhrchemie A. G., Sterkrade. A fresh-water KG calcined at 700° C.	U

[1] Micropores have diameters less than 5 microns and macropores diameters greater than 5 microns.

TABLE 58.—*Chemical analyses of kieselguhrs*

	Filter-Cel	Filter-Cel, acid-extracted	Hyflo Super-Cel	Dicalite 911	Portuguese	German
	Weight percent as elements					
Aluminum	1.87	0.9	1.90	2.29	2.06	0.58
Iron	.85	.49	.87	1.49	.87	3.86
Phosphorus	.10	(1)	.07	.01	.006	.01
Titanium	.13	(1)	.12	.16	.08	.08
Calcium	.31	(1)	.19	.46	.03	.27
Sulfur	.03	(1)	.03	.09	.05	.19
Loss on ignition, weight percent	3.47	.60	.33	4.28	1.58	1.66

[1] Not determined.

A sample of Filter-Cel was extracted for several hours with hot nitric acid, washed and dried, and finally heated at 650° C. The extraction decreased the percentages of aluminum and iron to about half. The weight-loss-on-ignition data indicate that Hyflo Super-Cel, acid-extracted Filter-Cel, and Portuguese and German kieselguhrs have probably been heated to 600° C. or higher.

The electron micrographs of Filter-Cel show it to be composed chiefly of thin plates and rods. The plates, which appeared to be portions of the disklike valves of diatoms, had irregular outlines, the longest and shortest dimensions averaging about 5 and 3 microns. The plates were thin enough to be translucent to electrons. The plates were covered with circular holes about 0.5 micron in diameter, and some fine structure to diameters of less than 0.1 micron was visible. The rods were about 1 micron in diameter and 5 to 15 microns in length.

Acid extraction and calcination had no apparent effect on the Filter-Cel as indicated by the electron micrograph; but the surface area decreased slightly, and the bulk density was higher.

The Hyflo Super-Cel also had a plate and rod structure; however, both plates and rods were larger than in Filter-Cel. The fine structure found in Filter-Cel was not present. The outline of the Hyflo Super-Cel particles was irregular. This irregularity, together with the porous structure of the plates, accounted for the low bulk density of Filter-Cel and extracted Filter-Cel.

Dicalite 911 was characterized by rods, perforated disks about 8.0 microns in diameter, and elliptical particles. There was a considerable amount of fine structure with holes averaging about 0.3 micron in diameter, and the surface area was larger than that of the other kieselguhrs reported here. The pore volumes of this material reflect the more compact structure of Dicalite 911, compared with Filter-Cel.

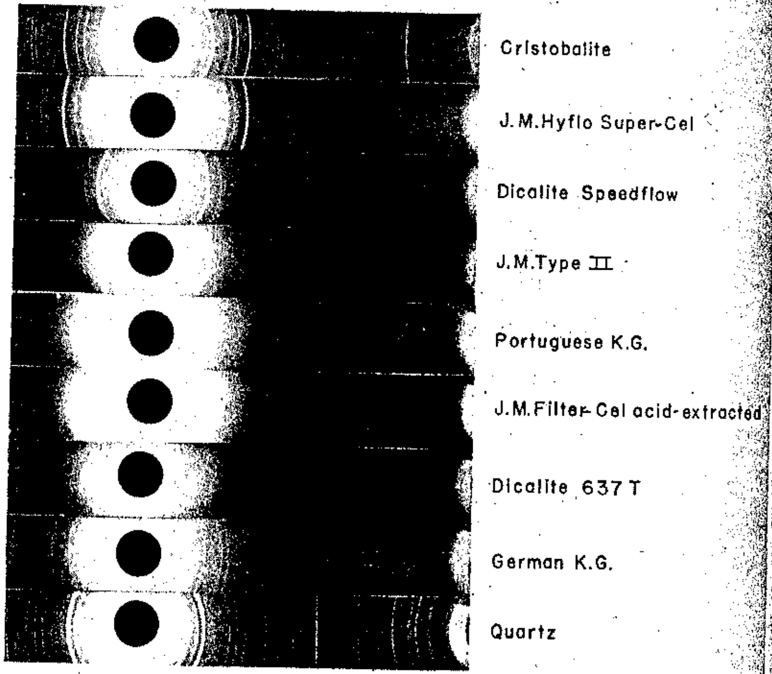

FIGURE 42.—X-ray diffraction patterns of various kieselguhrs, quartz, and cristobalite.

The Portuguese kieselguhr was considerably broken into small, regular pieces. The most common unbroken forms had a circular cross section, and at least some of these appeared to be porous spheres. There was only a small fraction of plate and rod forms. The circular structures averaged about 4 microns in diameter and the smaller pieces about 1×2 microns. The particles probably had considerable fine structure, for the particle diameter calculated from surface area was about 0.2 micron, assuming cubic or spherical particles. The particles appeared thicker than the disks in Filter-Cel and were more irregular in shape, which accounted for the higher bulk density of this material.

The German kieselguhr was taken from the catalyst-testing factory, Ruhrchemie A. G., Sterkrade. The diatoms of this material were the most perfect of any encountered in this study. The most prominent forms were disks and perforated rods or "ladders." The disks had diameters of about 6 microns, with holes averaging about 0.05 micron in diameter. The rodlike structures averaged about 5×15 microns, with holes 0.3 to 0.5 micron in diameter. Due to the proportion of elongated structures and rather perfect disks, the bulk density of this sample was very low, and both the macro- and micro-pore volumes were large.

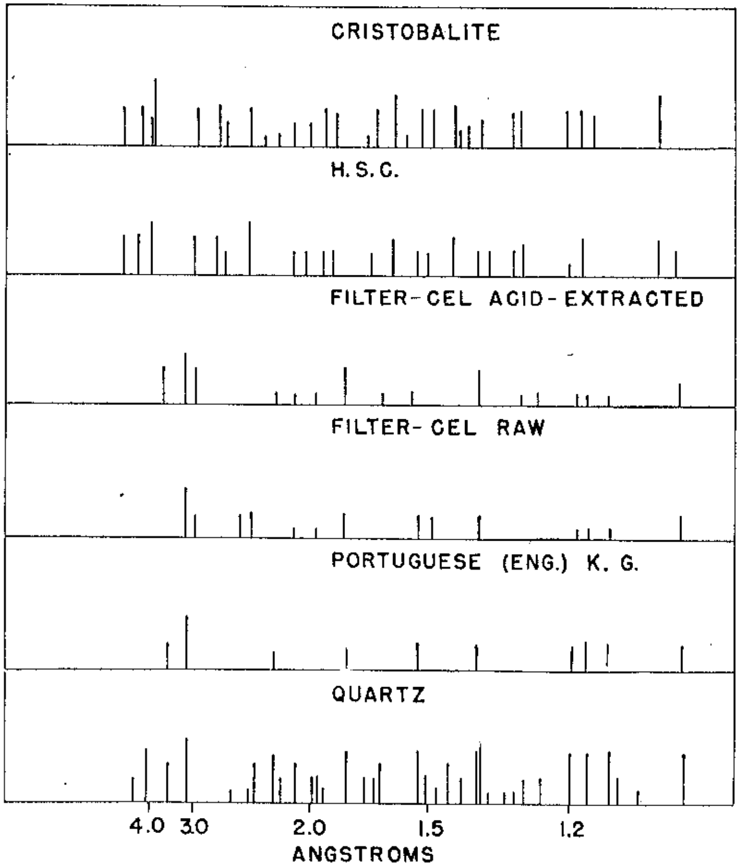

FIGURE 43.—X-ray diffraction analysis of various diatomaceous earths.

X-ray diffraction studies were made of Filter-Cel, acid-extracted Filter-Cel, Hyflo Super-Cel, Dicalite 911, and Portuguese and German kieselguhrs. The diffraction patterns are shown in figure 42, and the intensities of the lines are plotted in figure 43, where the patterns are compared with known samples of β quartz and β cristobalite. These two compounds and, in addition, γ tridymite, are the three forms of crystalline silica that exist at room temperature. There is also a large number of amorphous forms of silica, such as hydrous opaline silica, vitreous silica, and chalcedony.

The Portuguese kieselguhr proved quite amorphous, with only a few faint lines showing, which on comparison corresponded, line for line, with the strong lines of β quartz. This material may be assumed to be amorphous silica with less than 25 percent of microcrystalline β quartz. Filter-Cel contained many of the same lines as Portuguese kieselguhr and, in addition, some unidentified lines. Acid-extracted Filter-Cel was also largely amorphous. It still showed some of the unknown lines found with raw Filter-Cel, although these seemed weaker. The acid-extracted Filter-Cel also showed lines in addition to those of raw Filter-Cel, and these were identified as β quartz. Dicalite 911 was quite amorphous and had a diffraction pattern similar to Portuguese and Filter-Cel kieselguhrs.

Hyflo Super-Cel showed a well-developed crystal structure whose lines corresponded with β cristobalite. Although cristobalite is not thermodynamically stable at any temperature to which the Hyflo Super-Cel was subjected in its preparation, it rather than the expected tridymite was formed because of the peculiar kinetics of the formation of cristobalite. The German kieselguhr gave a quartz diffraction pattern that was more distinct than the patterns of Portuguese or Filter-Cel kieselguhrs. This was probably due to the calcination. As cristobalite was not present, it may be inferred that the sample had not been heated above 870° C., the upper limit of the stability of quartz.

In table 59 are presented several properties of unreduced cobalt catalysts, including the type and surface area of the kieselguhr used, surface areas of catalysts, percentage of cobalt, mercury, and helium densities, and micro pore volumes. The nitrogen isotherms of the unreduced cobalt catalysts were of the usual S-type with only a slight amount of hysteresis indicating a system of pores of which the majority was larger than 500° A. The bulk of the area of the catalyst was that of the "cobalt oxide complex" [96] and not the kieselguhr. Unreduced Hall catalysts had areas varying from 78 to 110 square meters per gram, while the unreduced Fischer catalyst 108B, which contained more cobalt, less kieselguhr, and no magnesia had areas of 66.5–84.1 square meters per gram.

Electron micrographs of pelleted unreduced Hall- and Fischer-type catalysts which had been gently crushed in a mortar showed clumps of cobalt oxide complex of varying size, alone and covering and filling the kieselguhr particles, and particles of kieselguhr almost free of cobalt oxide complex. A representative micrograph of Fischer catalyst 108B at a magnification of 5,400 is shown in figure 41–f. It is interesting to note that although the kieselguhr comprised about one-third of the catalyst by weight, only a small portion of it is visible. The outline of the clumps of cobalt oxide complex were very feathery, indicating that these were probably clusters of tiny particles. This agrees with the surface area of the catalyst being several times that of the kieselguhr. No well-defined crystal faces or edges were observed in any of the micrographs. Similar results are reported by Turkevich [97] for a nickel–thoria–kieselguhr catalyst.

TABLE 59.—*Properties of unreduced Fischer-Tropsch catalysts*

Catalyst	Form[1]	Kieselguhr	Area of kieselguhr, m.²/g.	Area of catalyst, m.²/g.	Cobalt, percent	d_{Hg}	d_{He}	Micropore volume, cc./g.
Hall ($Co:ThO_2:MgO:KG=100:6:12:200$):								
89–H	P	Hyflo Super-Cel	1.9	67.2	23.9	1.20	2.74	0.47
89–I	G	do	1.9	83.9		.51	2.75	1.60
	P	do	1.9	75.2	23.7	1.27	2.75	.43
89–J	G	Filter-Cel	22.2	104.1		.43	2.76	1.97
	P	do	22.2	84.1	24.5	.97	2.77	.67
89–K	G	Portuguese	17.5	101.1		.61	2.75	1.28
	P	do	17.5	88.8	24.6	1.20	2.75	.47
89–U	G	German	14.9	109.3		.445	2.75	1.89
	P	do	14.9	86.3		1.10	2.75	.55
89–V	G	Dicalite 911	29.3	101.9		.544	2.75	1.47
	P	do	29.3	77.6		1.31	2.75	.40
MC–15	G	None		149.0		.676	3.80	1.22
Fischer ($Co:ThO_2:KG=100:18:100$):								
108–B	G	Filter-Cel	22.2	84.1		.481	3.08	1.76
	P	do	22.2	71.6	34.0	1.13	3.08	.56
	LP	do	22.2	66.5		1.51	3.08	.34

[1] G=broken filter cake; P=⅛-in. x ⅛-in. (diameter) pellets; LP=¼-in x ⅛-in. (diameter) pellets.

The surface areas of the catalysts are not additive with respect to the kieselguhr used. Catalysts prepared from flux-calcined Hyflo Super-Cel have lower surface areas than those prepared from natural kieselguhrs.

The bulk density of the catalysts reflects the bulk density of the kieselguhrs used. In granular catalysts, the density varied directly with the bulk density of the kieselguhr, while the density of the pelleted catalysts appears to be functions of the kieselguhr and the pelleting, which is not always reproducible. The bulk volume of an amount of granular catalyst containing 1 gram of kieselguhr was nearly equal to the bulk volume of a gram of kieselguhr. When the catalyst was pelleted, the bulk volume was less than that of the kieselguhr that it contained.

In table 59 are given the surface areas and pore volumes of several unreduced cobalt catalysts in granular and pelleted forms. In every instance the surface areas of the pelleted catalysts were less than the corresponding granules. The average pore diameter, *d*, calculated for cylindrical open-end pores from the micropore volume, V_{micro}, divided by the surface areas, *A*, where $d=4\ V_{micro}/A$, was about 250° A. for pellets and 800° A. for granules. MC15 which contains no kieselguhr had pores of 330° A., average diameter in the granular form. From the data presented and others, the following concept of the cobalt catalysts is given. The kieselguhr in the catalyst acts as a "brushpile" into which the particles of cobalt oxide complex may be placed without increasing the bulk volume. The cobalt oxide complex is composed of clusters of much smaller particles than the kieselguhr, and these particles probably almost completely cover the

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[96] "Cobalt oxide complex" as used in this paper means the mixture of cobalt oxides and promoters; that is, everything except the kieselguhr.

[97] Turkevich, J., Electron Microscopy of Catalysts: Jour. Chem. Phys., vol. 13, No. 6, 1945, pp. 235–239.

kieselguhr so that the total surface may be that of the cobalt oxide complex. In pelleting the small particles of the complex are pressed together so that some of their surface disappears.

Upon reduction, these catalysts sinter to varying degrees, depending, among other factors, upon the promoters present and the extent and duration of reduction. The presence of promoters makes reduction more difficult and reduces the amount of sintering. Thus, a cobalt oxide powder can be quite completely reduced in 24 hours at 250° C. in a slow stream of hydrogen with a change in surface area from 68.0 to 3.2 square meters per gram, whereas reduction of Hall catalyst 89H in a slow stream of hydrogen at 300° C. for 40 hours is only 65 percent complete with a change in surface area from 67.2 to 49.5 square meters per gram.

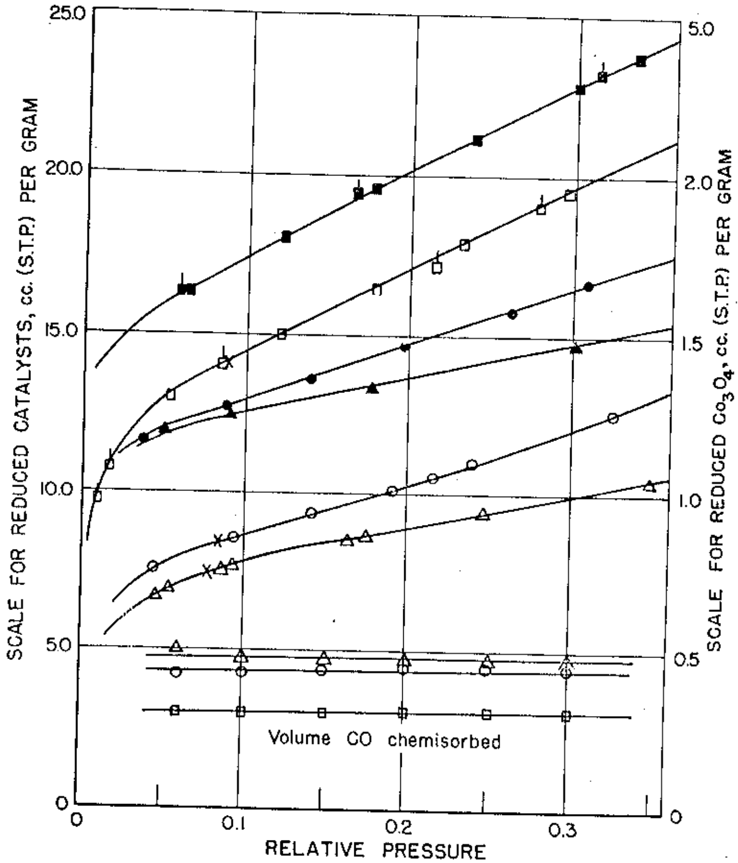

FIGURE 44.—Sorption of nitrogen and carbon monoxide at −195° C. on reduced pelleted catalysts 89H and 89J and reduced cobalt oxide powder where open points represent nitrogen and solid points represent carbon monixide isotherms. Points of reduced 89H are given by ○, two samples of reduced 89J by □ and □, and the reduced cobalt oxide by △. The volumes of chemisorbed carbon monoxide are given in the lower part of the graph.

The fraction of metallic cobalt in the surface has been estimated by the chemisorption of carbon monoxide at −195° C. The carbon monoxide isotherm is a composite of physical and chemisorption, the chemisorbed monolayer being formed at very low pressures, the physically adsorbed layers forming on top of this, as though the chemisorbed layer were not there. Since the properties of nitrogen and carbon monoxide related to physical adsorption are nearly identical, the nitrogen isotherm very nearly approximates the carbon monoxide isotherm. The difference between the two isotherms is the chemisorbed carbon monoxide.

In table 60, data are given on the reduction of cobalt catalysts, total surface areas, and the chemisorption of carbon monoxide on reduced Hall catalysts 89H and 89J, Fischer catalyst 108B, and cobalt oxide powder. The most common reduction procedure is reduction at 360° or 400° C. in a rapid stream of hydrogen, $SVH=6{,}000$ for 2 hours. This method at 400° C. reduced both Hall 89H and Fischer 108B catalysts quite completely. The total area for the 89J drops from 81.4 to 62.0 square meters per gram, while the area of 108B drops from 84.6 to 28.3 square meters per gram. Carbon monoxide and nitrogen isotherms were determined on catalysts 89H and 89J reduced by the rapid method at 400° C. The data are plotted on a relative pressure basis (the pressure of adsorbate divided by the condensation pressure) in figure 44. The carbon monoxide isotherm is equidistant above the nitrogen isotherm, the difference being the volume of chemisorbed carbon monoxide. The "X" on the nitrogen isotherms is the volume of gas necessary to form a physical monolayer as determined by the B. E. T. equation.[98] [99]

The presence of promoters in a catalyst retards sintering and makes reduction more difficult. Thus, the decrease in area upon reduction is the least with the doubly promoted 89 catalysts, greater with singly promoted Fischer catalyst, and greatest with cobalt oxide powder.

TABLE 60.—*Adsorption of nitrogen and carbon monoxide at −195° C. on unreduced- and reduced-cobalt catalysts and cobalt oxide*

Catalyst	Reduction method			Loss weight, percent	Surface area, m.²/g.[2]	V_m nitrogen, cc./g.[2]	V_{chemi} carbon monoxide, cc./g.[2]
	Temperature, ° C.	Hours	Space velocity/hour[1]				
89H				0.0	67.2	15.4	0.0
89H	400	2	6,000	17.9	36.9	8.4	4.3
89J				.0	84.1	19.2	.0
89J	400	2	6,000	17.7	62.0	14.2	3.1
108B				.0	84.6	19.3	.0
108B	400	2	6,000	28.6	28.3	6.5	
Co_3O_4				.0	68.0	15.4	.0
Co_3O_4	250	41	100	30.6	3.2	.74	.48

[1] Volumes hydrogen per bulk volume of catalyst per hour.
[2] All adsorption data per gram of unreduced catalyst.

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[98] Work cited in footnote 85, p. 158.
[99] Work cited in footnote 86, p. 158.

The amount of carbon monoxide chemisorbed on the reduced cobalt oxide was smaller than anticipated. On iron[1] and nickel[2] the chemisorbed carbon monoxide usually exceeded the physically held monolayer by 30 percent or more. However, Emmett[3] found that carbon monoxide chemisorbed to less than a monolayer on highly sintered iron powders. This may be due to chemisorption of carbon monoxide molecules on one atom preventing chemisorption on adjacent atoms due to steric effects. Another possible explanation is the accumulation of traces of impurities on the surface. It is interesting to note that in the reduction the metal formed into hexagonal platelets with edges of about 6 microns, many times the size of the unreduced particles. Catalyst 89J chemisorbed less carbon monoxide than 89H, while 89J was the more active. This may mean that the active portions of the surface are not metallic cobalt or that these surfaces are significantly different.

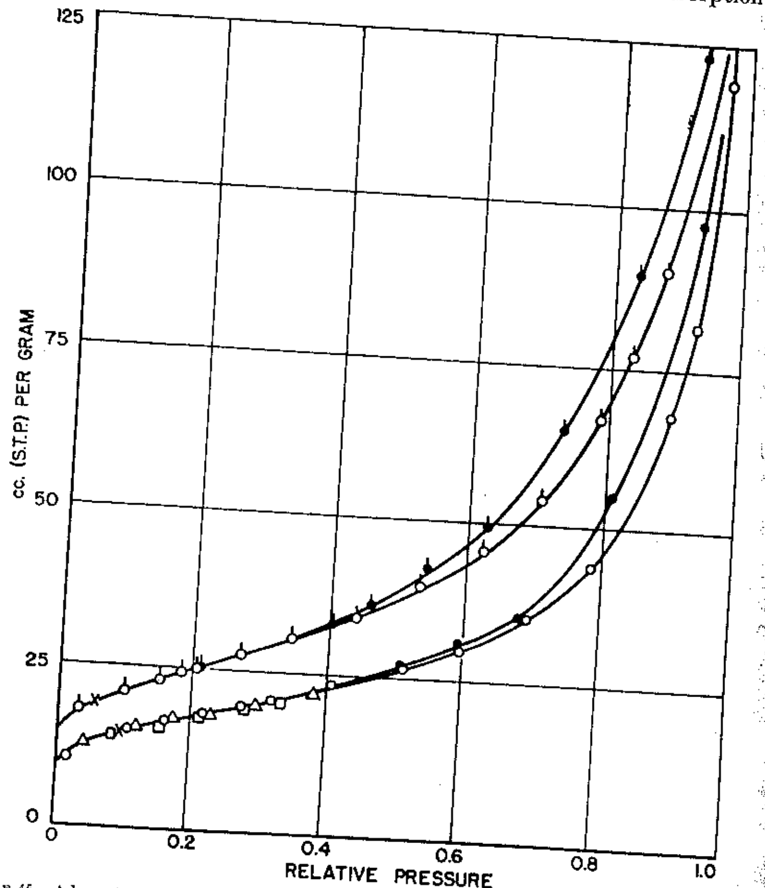

FIGURE 45.—Adsorption of nitrogen at −195° C. on unreduced- and reduced-cobalt catalyst 89J, where ○ represents the unreduced catalyst and ○, □, and △ represent different samples of reduced catalyst. Desorption points are solid, and the volume of gas corresponding to a monolayer is represented by X.

In figure 45, nitrogen isotherms at −195° C. on catalyst 89J are presented for the original and reduced catalysts. Both isotherms indicate a capillary system in which the majority of the pores are greater than 500Å. in diameter, since the isotherms show no tendency to flatten at the highest pressures measured. The slight amount of hysteresis of the isotherms indicates the presence of some pores in the range of 16–60A. in diameter.

A limited number of experiments indicates that probably all of the 89-type catalysts sinter about an equal amount with the standard reduction procedure. It is possible therefore that some significant correlation may exist between activity in the synthesis of reduced catalysts with total surface area of the unreduced catalyst. Two methods of correlation were used: (1) Surface areas of unreduced catalysts per cubic centimeter were compared with the temperature necessary to give a contraction of 70 percent at space velocities of 100 (volumes of synthesis gas per volume of catalyst per hour); (2) surface areas of unreduced catalyst per gram were correlated against the temperature required to produce a contraction of 70 percent at inflows of synthesis gas of 150 cubic centimeters (S. T. P.) per hour per gram of unreduced catalyst. Plots of these types are given in figure 46, *A* and *B*. A graph of type A is strongly dependent on the weight of catalyst per charge, while a plot of type B depends only on surface area. In most of the catalyst testing the space velocity was maintained at about 100, and the average temperature plotted against surface area per cubic centimeter gave a correlation of type A, as shown in figure 46, *A*. With most pelleted catalysts the flow of synthesis gas per gram was about 150 cubic centimeters per gram per hour, but on granular and some pelleted catalysts the flow differed considerably from this value. All the temperatures were corrected to those corresponding to flows of 150 cubic centimeters per gram per hour with the Arrhenius equation.[4] With pelleted catalysts this correction is quite small, but it is quite large with granular catalysts. In both plots an inverse relationship exists between activity and surface area. The triangles, which represent catalysts prepared with calcined kieselguhrs, Hyflo Super-Cel, and German kieselguhrs, fall into a fairly good straight line, while the circles representing natural kieselguhrs can be grouped within a rather narrow band, with the exception of points for tests 22 and 38. Positions of the points along the lines are different in the two plots, but the relative position of the lines is the same.

The following interpretations may be placed on the data: (1) The catalysts prepared from calcined kieselguhrs were less active when compared at equal surface areas (and also equal weight) than those prepared from natural kieselguhrs; (2) granular and pelleted forms of the same catalyst showed about the same variations in activity with surface area as different pelleted catalysts. The pore volumes

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[1] Work cited in footnote 88, p. 158

[2] Work cited in footnote 89, p. 158.

[3] Emmett, P. H., communication to authors.

[4] $\frac{d \ln Q}{dT}=\frac{E}{RT^2}$, where ln=natural logarithm, Q=flow rate, T=absolute temperature, R=2 calories, and E=24,000 calories as determined in experiments reported in an earlier part of this paper.

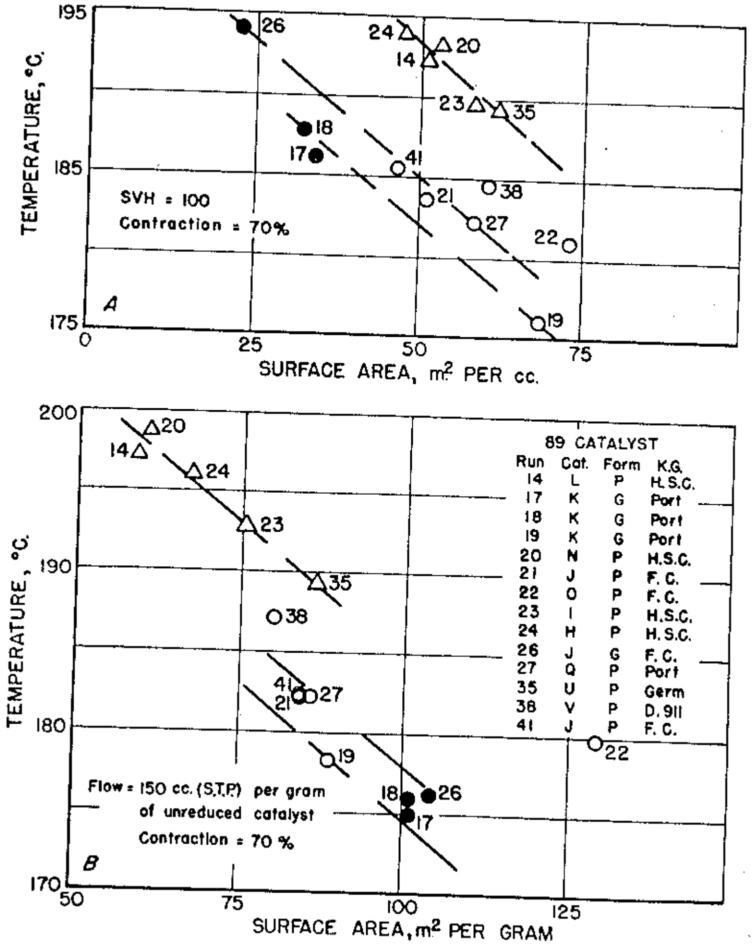

FIGURE 46.—Variation of activity of reduced-cobalt catalysts of the 89 series with surface areas of unreduced catalysts. In part *A*, temperature of operation at a space velocity per hour of 100 is taken as a measure of activity and is plotted against surface area per cubic centimeter of catalyst. In part *B*, temperature of operation at a flow of in-gas of 150 cc. per gram of unreduced catalyst is plotted against surface area per gram of unreduced catalyst. Catalysts containing natural kieselguhrs are represented by ○ and those with calcined kieselguhrs by △. Pelleted catalysts are given by open points and granular catalysts by solid points.

of the granular catalyst were three to four times those of the pellets; this implies that diffusion was not an important factor and that most of the surface was available to the reactants. This is not unexpected, since the flow rates were low and the pores relatively large.

The activity decreases upon pelleting to an amount corresponding to the decrease in surface area. Pelleting also causes a change in the distribution of products. Pelleted catalysts produced more methane, C_1–C_4 hydrocarbons, and carbon dioxide than corresponding granular catalyst, as shown in table 47.

IRON FISCHER-TROPSCH CATALYSTS

Many of the iron catalysts prepared and tested by the Bureau of Mines were pure hydrated ferric oxide precipitated from hot solutions of ferric nitrate or chloride with potassium carbonate or hydroxide solutions. The catalysts were washed thoroughly but may still contain traces of alkali or other components of the solution. Catalysts prepared from ferric nitrate were active, while those prepared from ferric chloride were inactive.

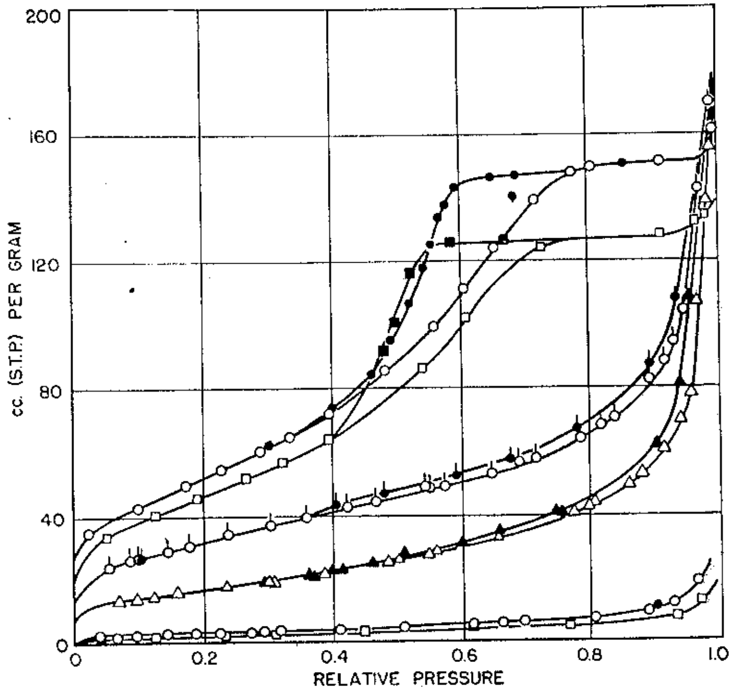

FIGURE 47.—Adsorption of nitrogen on unreduced- and reduced-iron catalysts at −195° C. where 10K, unreduced and reduced, are □; 47C, unreduced and reduced, ○; 47D, unreduced, ⌀; and 80A, unreduced, △. Desorption points are solid.

Nitrogen isotherms at −195° C. determined on several unreduced and reduced nitrate- and chloride-type catalysts are shown in figure 47, with data for these isotherms in table 61. The total surface areas for most of the unreduced iron catalysts are somewhat higher than those of the cobalt catalysts, but the cobalt catalysts contain about one-third to one-half kieselguhr, which has an area much smaller than the other materials in the catalyst. The area of the cobalt oxide complex per gram of complex is of the same order as that of the iron catalysts. The isotherms of catalysts 10K and 47C indicate that these samples have a gellike structure with very fine pores such as present in silica gel.[5] The flattening of these isotherms at high relative pressures indicates complete filling of almost all of the pores. An estimate of the pore diameter may be obtained from the volume

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[5] For a bibliography of adsorption work on hydroxide gels see, Cohan, L. H., Hysteresis and the Capillary Theory of Adsorption of Vapors: Jour. Am. Chem. Soc., vol. 66, 1944, pp. 98-105.

of adsorbate required to fill the pores calculated as liquid, V_L, and the surface area, A, from the ratio of pore volume to surface area. For a cylindrical pore, $d=4V_L/A$, where d is the pore diameter.[6] The average pore diameters calculated on this basis for 10K and 47C are less than 50 Å. The strong hysteresis of these isotherms is also indicative of a gellike structure. The other samples 47D and 80A do not flatten at high relative pressures and have only slight hysteresis.

TABLE 61.—*Properties of original and reduced iron catalysts*

Catalyst	Unreduced			Reduced		Activity
	Area m.²/g.	Average pore diameter, Å.	X-ray pattern [1]	Area m.²/g.	Loss, weight percent	
10K [2]	169.1	46.8	Very diffuse	9.0	8.2	Active.
47C [3]	195.5	48.6	do	11.3	13.4	Inactive.
47D [3]	120.1		do			Do.
80A [2]	59.1		Sharp			Active.

[1] See table 53 and figs. 33, 34, 35, and 36.
[2] Precipitated from ferric nitrate solution.
[3] Precipitated from ferric chloride solution.

The isotherms of the unreduced catalysts are quite similar for samples precipitated from either ferric chloride or nitrate, the catalysts prepared from ferric chloride having slightly higher areas on the few samples for which areas are available. Some agreement exists between the intensity of lines on X-ray diffraction patterns shown in figure 37 and the surface areas in that the X-ray diffraction patterns of catalysts with high areas are very diffuse and the lines of a lower area catalyst are sharp.

To account for the inactivity of the catalysts prepared from ferric chloride, it was thought that these catalysts might sinter more severely in reduction or pretreatment than those prepared from ferric nitrate, but surface-area measurements of reduced catalysts 10K and 47C show the sintering to be almost equal. The catalysts were reduced by a slow method in which the temperature is slowly raised to 360° C. in a slow stream of hydrogen and held for 4 hours at this temperature. The weight loss in the reduction corresponds approximately to the conversion of $Fe_2O_3 \cdot H_2O$ to Fe_3O_4. The surface areas decreased to about 5 percent of their former value. This degree of sintering is rather striking, but it is of the same order of magnitude as the sintering of the cobalt oxide powder, which was also unpromoted. After reduction the isotherms show no indications of a gellike structure. These areas, after reduction, are within the range of surface areas of reduced iron synthetic ammonia catalysts. The fact that no pronounced differences in the surface area occur between the chloride and nitrate type reduced and unreduced iron catalysts gives added interest to the X-ray and magnetic studies of iron catalysts described in an earlier section of this paper. However, it is possible that the inactivity of the catalysts prepared from ferric chloride is due to adsorbed chloride ions. As yet no carbon monoxide isotherms have been determined on iron catalysts.

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[6] 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.

APPENDIX ON PREPARATION OF CATALYSTS

Three methods for preparing catalysts were used, namely, precipitation as oxides or carbonates, impregnation of a carrier with the metal nitrates and subsequent roasting, and ignition of the nitrate or sulfate. The precipitation method was used in 80 percent of the catalyst preparations. Its use involved the study of a number of variables, among them: (1) Nature of reagents, (2) concentration of solutions, (3) temperature of precipitation, (4) rate of precipitation, (5) method and extent of washing the precipitate free from electrolytes, (6) extent of drying the precipitate, and (7) final formulation into particles of the desired size.

The total number of catalyst preparations tested in the laboratory-size converters was 62. Twenty-two were unpromoted iron catalysts, 21 promoted iron, and 19 cobalt, nickel, or cobalt-nickel combinations. The 22 unpromoted iron catalysts included 7 preparations of catalyst 10, 4 of catalyst 47, 3 of catalyst 50, 2 of catalyst 68, and 1 preparation each of 6 other catalysts (48A, 49A, 69A, 70A, 80A, and 81A). Of the 21 promoted iron catalysts, there were 18 different catalysts (1E, 5A, 6A, 9A, 11A, 15A, 20A, 21A, 22A, 23A, 25A, 39A, 40A, 43A, 44A, 51A, 67A, and 85A), 2 preparations of catalyst 24, and a 234 Ruhrchemie preparation captured in Germany. In the third group there were 9 preparations of catalyst 89 and 1 batch each of 10 other catalysts (2A, 12B, 36A, 38A, 60A, 61A, 62A 64A, and 108B).

Each catalyst prepared from different starting materials received a number, while letters were assigned to different batches of the same catalyst. For example, the designation 10D referred to the fourth preparation of the tenth catalyst.

PREPARATION OF UNPROMOTED IRON CATALYSTS

Details for the individual catalysts are given in tables 16 and 17. Fifteen of the unpromoted iron catalysts were precipitated as the hydrous ferric oxide (10A, B, C, D, F, K, M, 47A, C, D, F, 48A, 68B, 80A, and 81A); 3 were ignited to the oxide (50C, 69A, and 70A); and 4 were iron oxides which were used untreated (49A, 50A, B, 68A).

In the precipitation method the following general procedure was used: To a hot solution of the iron salt was added a cold solution of the precipitant in slight excess. The precipitated slurry was washed 12 to 16 times by decantation with distilled water, until the wash water showed a negative test for nitrate or chloride. After the fifth or sixth washing in this manner, part of the catalyst became colloidal and remained suspended in the supernatant liquid. When this occurred, addition of a small amount of ammonium hydroxide (1.5 to 2.5 cubic centimeters) or 10 percent ammonium nitrate solution (3 to 5 cubic centimeters) was effective in coagulating the precipitate. After suction filtration, the precipitate was spread on glass plates in cakes approximately ¼ inch thick, air-dried at room temperature to a hard product dry to the touch, and finally oven-dried for 15–17 hours at 145°–150° C. The dry cake was ground in a mortar and sifted through a 60-mesh screen. The crushed catalyst was mixed with four percent powdered graphite, as lubricant, and compressed into pellets ⅛ inch in diameter by 3/32 inch in length.

Preparation by ignition involved varying procedures. In one case (69A), roasting took place in the muffle oven; in 70A, a coater was used during the ignition.

PREPARATION OF NO. 10 CATALYSTS

The seven preparations of the No. 10 catalyst, batches A, B, C, D, F, K, and M, were precipitated by potassium carbonate from ferric nitrate solution. The concentration of the iron solutions ranged from 0.6 to 1.2 moles $Fe(NO_3)_3 \cdot 9H_2O$ per liter of water. The solution of the precipitant contained approximately 4 moles of anhydrous K_2CO_3 per liter of water. Precipitating temperatures ranged from 65° to 83° C., and the time consumed in adding the precipitant ranged from less than 5 to 30 minutes. The appearance and volume of the slurry changed with the temperature and rate of precipitation. Temperatures below 70° C. and rapid precipitation usually produced a deep red-brown voluminous precipitate. Dense, light red-brown to tan precipitates were obtained with temperatures of 80° C. and higher and slow addition of precipitant. Catalysts 10B, 10F, and 10K were deep red-brown and bulky; 10A, 10C, and 10D were lighter brown and slightly more dense. The exception to the observed correlation between conditions of precipitation and appearance was catalyst 10M. Although it was precipitated at the low temperature of 65° C. in 15 minutes, the slurry was not deep red, but chocolate brown. This difference probably was due to the presence of chloride ion in the ferric nitrate solution before the precipitant was added. Catalyst 10M is comparable in appearance with the 47 series of catalysts, which were precipitated from ferric chloride solution.

The No. 10 catalysts were washed by the decantation method until the wash water gave a negative nitrate test with diphenyl amine-sulfuric acid reagent. The volume of each washing was equivalent to the volume of the precipitated catalyst. In the early preparations the temperature of the wash water was 80° C. or higher, but where it was desired to retard "aging" of the catalyst, this temperature was lowered to 65° C. Catalyst 10M showed a faintly positive chloride test, even after 16 washings. The total quantity of wash water per gram of Fe_2O_3 ranged from 0.24 liter for 10B to 0.64 liter for 10D.

Immediately following filtration, parts B and C of catalyst 10B were oven-dried. All the other preparations of catalyst 10 were air-dried for an average period of 125 hours at room temperature before oven-drying. In the oven, 10A was dried at 105° C. and 10F, part A, at 85° C.; all the other preparations at 150° C. for approximately 20 hours. It was observed that part C of 10F, oven-dried at 149° C., lost 4 percent more weight than 10F, part A, dried at 85° C.

The dried catalyst preparations were gellike in appearance, hard, black, and lustrous, with conchoidal fracture. Catalysts 10D and 10M were dark brown and somewhat dull at the fracture. Yields of dry cake, compared with a theoretical yield assumed to be Fe_2O_3, calculated from starting material, averaged 103 percent, indicating that some water was held in combination with the oxide. The crushed products, mixed with powdered graphite, were compressed into hard, well-formed, dark-brown pellets with an average bulk density of 1.3 grams per cubic centimeter at maximum packing. 10M had a low pellet bulk density of 0.93 gram per cubic centimeter. A portion of 10K dried cake was cracked into 8- to 14-mesh granules, whose bulk density was 1.17 grams per cubic centimeter.

PREPARATION OF NO. 47 CATALYSTS

Four batches of the No. 47 catalyst—A, C, D, F—were tested for activity in the laboratory-size converters. In this group hydrous ferric oxide was precipitated from ferric chloride solution, in concentrations ranging from 0.5 to 0.8 mole $FeCl_3 \cdot 6H_2O$ per liter of water, by potassium carbonate dissolved in water in the ratio of approximately 35 moles of anhydrous K_2CO_3 to 1 liter of water. Precipitating temperatures of about 75° C. and rapid addition of the carbonate solution yielded bulky, chocolate-brown precipitates. 47A and 47D were precipitated at a higher temperature and were tan-colored in the wet state. Catalysts 47C and 47F were chocolate brown and more bulky than 47A and 47D. In general, the precipitates of the 47 series contained more yellow material than the No. 10 catalysts.

The catalysts were washed approximately 17 times by decantation, with a volume of wash water equal to the volume of the precipitate. The tan precipitates became colloidal after only three or four washings and required the addition of 3 to 5 cubic centimeters of 10-percent ammonium nitrate solution for coagulation. The total quantity of wash water per gram of Fe_2O_3 ranged from 0.28 liter for 47A to 0.53 liter for 47D. In each preparation the supernatant liquid showed a positive chloride test, even after 17 washings.

Following filtration, all the No. 47 catalysts were air-dried for about 90 hours and then oven-dried at about 150° C. The dried catalysts were dark brown, and not as hard and lustrous as those of the No. 10 series. Catalyst 47D, which was formed by slow precipitation at relatively high temperature (85° C.), was light red-brown, soft in appearance, and not gellike. The yield of dry cake averaged 104 percent, assuming the theoretical to be the amount of pure Fe_2O_3 calculated from the starting material. This value was approximately the same as the average yield in series 10, indicating that water was still combined with the oxide even after drying at 150° C.

Compression of the crushed powder admixed with powdered graphite formed hard, dark-brown pellets. 47D pellets were formed with difficulty and were somewhat softer than in the other preparations. The average pellet bulk density of 47A, C, and D was 1.09 grams per cubic centimeter at maximum packing. This value was 15 percent lower than the average for the 10 series. 47F had an apparent bulk density of 1.38 grams per cubic centimeter which was in the range of the No. 10 catalysts.

PREPARATION OF NO. 50 CATALYSTS

Three batches of catalyst 50—A, B, and C—were tested in the laboratory-size converters. The raw material was a dark-rust powder obtained from the E. J. Lavino Co. of Lynchburg, Va. It was recovered from the sludge remaining after bauxite had been extracted and contained, in addition to iron oxide and alumina, titanium, zirconium, sodium, calcium, magnesium, and silica.

50A was composed of a sample of this material which had been powdered and sifted through a 60-mesh sieve, oven-dried at 149° C. for 18 hours, mixed with 5 percent by weight of powdered graphite, and compressed into $\frac{1}{8}$- by $\frac{1}{8}$-inch pellets. The pills were very dense, having a bulk density of 1.61 grams per cubic centimeter at maximum packing. Difficulty in obtaining hard pellets was experienced because the powder was rather incompressible.

In the second preparation, 50B, water-soluble impurities were removed by refluxing the sample for 40 hours with three fresh portions of distilled water until negative tests for chloride, nitrate, and sulfate were obtained in the wash waters. The oxide was then filtered on a suction filter and dried in the following manner: 24 hours at room temperature, followed by 19 hours in the electric drying oven at 150° C. The crushed product was sifted through a 60-mesh screen, mixed with 4-percent powdered graphite, and compressed into pills $\frac{1}{8}$ inch in diameter times $\frac{3}{32}$ inch in length. The pellets were hard, well-formed, and dark brown, with a bulk density of 1.61 grams per cubic centimeter.

Nitric acid (1 volume of water to 1 of concentrated acid, specific gravity 1.42, assay 70 percent) was used in catalyst 50C to dissolve the iron in the washed raw material remaining from 50B. The mixture was heated with stirring for 2 hours at 70° C. and then diluted with hot distilled water to a large volume, in order to facilitate suction filtration of the gelatinous mass. The filtrate was concentrated to a syrup and then evaporated to dryness. The resulting residue was dried for 14 hours at 85° C. in the electric drying oven, then powdered in a mortar and dried further for 15 hours at 151° C. Finally, the catalyst was passed through a 60-mesh screen, mixed with 4 percent by weight of powdered graphite, and pelleted. The pills were $\frac{1}{8}$ inch in diameter by $\frac{3}{32}$ inch in length, with a bulk-density value smaller than those of the two earlier preparations, or 1.48 grams per cubic centimeter.

PREPARATION OF NO. 68 CATALYSTS

Limonite ore, which consists of a mixture of goethite ($\alpha Fe_2O_3 \cdot H_2O$) and hematite ($\alpha Fe_2O_3$), was the raw material for the 68 series.

The sample in preparation 68A was powdered to pass through 60-mesh, dried 15 hours, and compressed into hard, well-formed pills, with a high bulk density of 1.75 grams per cubic centimeter. The lubricant was 4 percent by weight of powdered graphite.

In 68B powdered limonite ore was digested with 1:1 nitric acid for about 30 minutes. A black residue remained after filtration and was extracted with another portion of 1:1 nitric acid and filtered. The total residue, after drying for 2 hours at 120° C., represented 7 percent of the original undried ore. The two filtrates were combined, diluted with hot distilled water to a volume calculated to contain 0.3 mole of ferric nitrate per liter, and precipitated at 75° C. with potassium carbonate solution containing 3.5 moles of anhydrous K_2CO_3 per liter of water. A chocolate-brown slurry resulted, which was washed 16 times by decantation, with a wash volume equivalent to 1.5 times that of the precipitate. A total quantity of 0.53 liter of wash water per gram of Fe_2O_3 was used. The catalyst settled with unusual rapidity after each decantation washing and at no time tended to become colloidal. The hard, black, dried catalyst was similar in appearance to the ferric oxide gels of the 10 series. The pellets had an apparent bulk density of 1.40 grams per cubic centimeter at maximum packing.

PREPARATION OF OTHER UNPROMOTED IRON CATALYSTS

Of the six remaining catalysts of this series, 48A, 80A, and 81A were precipitated from ferric nitrate solution by sodium hydroxide, potassium hydroxide, and sodium carbonate solutions, respectively. The conditions of precipitation were about the same as those already described in the preceding preparations. All three precipitates were chocolate brown at first, but the two catalysts precipitated by the strong alkalies gradually changed to tan during the subsequent washing period. Decantation washing with a 1:1 volume ratio of water to catalyst was followed in the usual manner by air- and then oven-drying at 150° C. Catalyst 81A dried to the hard, black gel similar to those of the 10 series. However, the other two catalysts when dry were brown and dull at the broken edges. The hard, dark-brown pellets showed differences in bulk density similar to those previously observed in comparison of the pellets of the gellike 10 series and the less gellike 47 series. Catalyst 81A had a bulk density of 1.3 grams per cubic centimeter, which was comparable with the 10 series, while catalysts 48A and 80A had a bulk density of about 1.1 grams per cubic centimeter. These values were of the same order as those of the 47 series.

The last three unpromoted iron catalysts were not precipitated ferric oxides. Catalysts 69A and 70A were prepared by igniting ferric sulfate and nitrate, respectively. In 69A powdered ferric sulfate was ignited for 12 days in a muffle oven at an average temperature of 550° C. During this period, 34 percent of the sulfate was converted to oxide. The apparent bulk density of the pelleted product was 1.30 grams per cubic centimeter at maximum packing. Catalyst 70A consisted of ferric oxide obtained by ignition of ferric nitrate in a "coater," which is an open revolving vessel mounted at a 45° angle and heated from below by a stationary burner. The nitrate melt was heated under 100° C. for 1 hour. The resulting dark-brown mass was mixed with about 50 cubic centimeters of water and heated to dryness under 100° C. This cycle was repeated twice until a bright red mass was obtained, which was ignited for 2 hours at 260° to 325° C. The red powder resulting from this treatment was so incompressible that it was pelleted with difficulty only after 3 percent gum arabic had been added as a binder. The pellets had an apparent bulk density of 1.40 grams per cubic centimeter at maximum packing. 49A was a catalyst prepared from sponge iron. The raw material, crushed to pieces of approximately 8-mesh particle size, was wetted with 6N nitric acid solution, then air-dried on a glass plate at room temperature 15 hours. Subsequently, the product was oven-dried at 150° C. for 14 hours. At this point the catalyst had gained 10 percent in weight. The material was again steeped in 6N nitric acid and oven-dried at 150° C. for 14 hours. No further gain in weight of the product was observed.

The final product consisting of pieces of 8- to 20-mesh size had an apparent bulk density of 1.75 grams per cubic centimeter at maximum packing.

PREPARATION OF PROMOTED IRON CATALYSTS

Details for the 20 catalysts in this group are indicated in tables 18 and 19. There were 14 two-component, 5 three-component, and 1 polycomponent iron catalysts. Of the singly promoted preparations 10 were iron–copper combinations, with the constituents present in the ratio of 4 iron atoms to 1 of copper. Catalysts 1E, 9A, and 11A were prepared from ferric and cupric nitrates; 5A from ferric chloride and cupric nitrate; 43A from ferric and cupric sulfates; 23A, 24A, 24C, and 25A from ferrous and cupric sulfates; and 85A from ferrous and cupric chloride. Two catalysts were thorium-promoted iron preparations. 15A, obtained from ferrous sulfate and thorium nitrate, contained the oxides in the ratio of 5 : 1; 51A, from ferric and thorium nitrates, contained a ratio of iron : thorium of 5 : 1. Catalyst 40A was prepared from ferric and zinc nitrates in the ratio of 4 iron atoms : 1 of zinc. Catalyst 44A contained ferric oxide and chromium trioxide in the ratio of 1 : 4, from ferric nitrate and chromium trioxide.

Of the five doubly promoted iron catalysts, 20A, 21A, and 22A were all prepared from the nitrate salts, each containing 4 atoms of ferric iron, 1 of copper, and 1 of a third constituent. In 20A the third component was zinc, aluminum in 21A, and chromium in 22A. 6A, from ferric chloride, ferrous sulfate, and cupric nitrate, contained the following atomic ratio: $Fe^{+3} : Fe^{+2} : Cu :: 8/3 : 4/3 : 1$. 67A was composed of 3 atoms of ferric iron, 2 of cobalt, and 1 of thorium, from the nitrates.

The polycomponent iron catalyst was 39A. It was the only iron catalyst prepared on a carrier and had the following composition: Iron and cobalt, from ferrous sulfate and cobaltous nitrate, were present in atomic ratio of 4 : 1; 4 atoms of iron plus cobalt were present for every atom of copper from cupric nitrate; the weight of Hyflo Super-Cel (alkali-treated and calcined diatomaceous earth) equaled that of the combined metal oxides.

All of the promoted iron catalysts were prepared by precipitation. Most of them were made by the standard general procedure adopted for the precipitated unpromoted iron oxides. The salts containing the promoter ion were introduced by dissolving them with the iron salt, so that the metal oxides were coprecipitated.

The concentration of the iron-plus-promoter solutions averaged 0.5 total mole of salt per liter of water; the concentrations of the precipitants ranged from 3.0 to 7.3 moles of anhydrous alkali per liter of water. Temperatures of precipitation varied over a 10° range from 70° to 80° C., and the time consumed in the addition of precipitant remained fairly constant at 20 to 30 minutes. These conditions were found not to be as critical for this group of preparations as for the unpromoted iron catalysts, and for this reason more latitude in temperature and rate of precipitation was permissible. The precipitant was added hot at approximately 80° C. in catalysts 1E, 5A, and 6A; it was added cold in the other preparations. In 24C and 85A, which were precipitated from ferrous salts, partial hydrolysis of the

iron solutions was observed at 75° C. before precipitant was added.

One variation of the standard procedure was to precipitate the catalyst constituents separately. In catalyst 9A the hydrous ferric oxide was precipitated by ammonium hydroxide and the promoter, cupric oxide, by ammonium carbonate. The two slurries were then mechanically mixed.

Three catalysts—11A, 25A, and 39A—were partly precipitated by sodium borate solution. In this procedure three-quarters of the total catalyst was precipitated in the usual manner. Each constituent in the fourth quarter of the catalyst was individually precipitated at room temperature by saturated (5 percent) sodium borate solution. The slurries so obtained were mixed with the balance of the precipitate. Catalyst 39A also contained a carrier, Johns-Manville Hyflo Super-Cel, which was introduced into the solution containing the major portion of the metal salts.

Another variation in preparation procedure was used in catalyst 44A. The iron oxide portion of the catalyst was precipitated in the usual fashion and washed by decantation eight times with a wash water:precipitate ratio of 3. Following vacuum filtration, the required quantity of chromium trioxide in a concentrated solution was mixed mechanically with the wet pressed cake of hydrous ferric oxide. A bright-red paste was obtained.

The precipitate volumes varied considerably; they ranged from 0.4 to 3.0 liters per 100 grams of total oxides. The ferric-iron-promoted catalysts were bulky and similar in volume to the unpromoted iron catalysts. However, the ferrous iron precipitates were nongelatinous and denser than those from ferric salts. Catalyst 43A, precipitated from a ferric salt, was an exception to the observed correlation; its volume was only 0.7 liter per 100 grams of oxides. In appearance most of the ferric iron catalysts were brown. The color of 5A, precipitated from ferric chloride, was light brown; 43A, from ferric and cupric sulfates, was rust-colored. All the catalysts precipitated from ferrous salts were black.

Washing was accomplished by the decantation method. Six to nineteen washings were given the catalysts in volumes that varied from a 1:1 water:precipitate ratio for ferric iron catalysts to a 5:1 water:precipitate ratio for ferrous iron catalysts. In the early preparations—as for example, in 1E, 5A, 6A, 9A, 15A, 20A, 22A, and 24A—the temperature of the wash water was 80° C., but it was later dropped to 65° C. The three catalysts partly precipitated by sodium borate solution were washed with water at room temperature. One of the ferrous iron catalysts (24A) was occasionally mixed by injection of a stream of air during washings. The quantities of wash water used per gram of metal oxides ranged from 0.23 liter in 20A to 0.68 liter for 6A.

The precipitates were filtered on a suction filter after the washing was completed. In 85A the wet-pressed filter cake was mixed with a concentrated solution of 0.12 percent of potassium carbonate, based on the weight of iron in the catalyst. The filtered catalysts were spread on glass plates in cakes approximately ¼-inch thick and in most cases were permitted to air-dry at room temperature until they were dry to the touch. A few preparations (as for example, 5A, 23A, 24A, 9A, 11A, 6A) were not air-dried, but slowly oven-dried to the top drying temperature of 150° C. Catalysts 25A, 39A, and 44A were immediately baked at 150° C.

Most of the ferric iron promoted catalysts were obtained as typical iron oxide gels, black, lustrous, and of conchoidal fracture. Catalysts 43A and 44A did not form black gels but were obtained as soft, friable rust cakes. The catalysts obtained from the ferrous salts were obtained as soft, dense, dark-brown, friable cakes. Data on the drying temperatures and times are summarized in table 19. The yields of dry catalyst averaged 103 percent, assuming the theoretical to be the sum of the metal oxides calculated from the starting materials.

To obtain the catalysts in a form ready for use in the converters, the dry cakes were powdered to pass through a 60-mesh screen, then mixed with 4 percent by weight of powdered graphite, and compressed into pellets ⅛ inch in diameter by ³⁄₃₂ inch in length. In a few cases slightly larger amounts of lubricant were used—6 percent in catalyst 9A, 5 percent in 44A. The pellet bulk density of the ferric iron preparations averaged 1.3 grams per cubic centimeter, which was in the same range as the average value for the No. 10 series of unpromoted iron catalysts. The ferrous iron catalysts were very compressible and formed hard, dark-brown pellets with an average bulk density of 1.5 grams per cubic centimeter, 15 percent more dense than the ferric iron catalyst pellets.

PREPARATION OF RUHRCHEMIE IRON CATALYSTS

The "best" iron catalyst used by Ruhrchemie[7] had the composition Fe:Cu:CaO:kieselguhr=100:5:10:30 and was prepared by dissolving iron and copper turnings, and calcium carbonate (or lime) in dilute nitric acid. The resulting solution contained, in grams per liter, 115 to 125 of iron, 5 to 7 of copper, and 11 to 13 of calcium oxide, and no excess of nitric acid. The iron was in the ferrous state. Before precipitation this solution was diluted with distilled water to lower the iron concentration to 36 to 55 grams per liter.

Precipitation was effected by introducing as quickly as possible the nitrate solution, heated to 98° C., into a boiling soda-ash solution (90 to 100 grams of soda ash per liter) while stirring vigorously. The quantity of soda ash used was such that at the end of the precipitation the pH was 6.8. The calculated amount of kieselguhr (30 parts by weight per 100 parts of iron) was then added to the mixture. The total time of precipitation must not exceed 5 minutes. The mixture was filtered rapidly and washed with hot water until the filter cake contained about 0.5 percent of sodium nitrate, based on the iron content. More complete washing was unnecessary, and in fact lowered the desired content of calcium oxide. About 200 to 220 cubic meters of wash water per ton of iron was sufficient.

After washing, the filter cake was repulped and enough potassium hydroxide added so that, after a subsequent additional filtration, 3.0 to 3.5 grams of KOH per 100 grams of iron was retained. This was achieved if the concentration of KOH in the mother liquor was about 6.0 grams per liter. After impregnation the suspension was filtered and the filter cake dried at 110° C., and subsequently shaped.

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[7] Work cited in footnote 88, p. 91.

The composition of sample 234, collected by W. F. Faragher,[8] was reported by him as Fe : Cu : CaO : kieselguhr= 100 : 2.5 : 10 : 15. This composition is somewhat different from that of the catalyst preparation described above.

PREPARATION OF COBALT AND NICKEL CATALYSTS

Details for the 21 catalysts in this series are summarized in tables 20 and 21. All the cobalt, nickel, and cobalt–nickel catalysts were supported on an inert carrier, which constituted at least 50 percent of the total product. In most of the preparations the carrier was diatomaceous earth, commonly known as kieselguhr, or an alkali-treated and calcined diatomaceous earth known by Johns-Manville's trade name of Hyflo Super-Cel. Other carriers included alumina pellets and sodium aluminosilicate gel. The metal constituents were grouped in the following manner: Cobalt promoted by thorium in five catalysts; cobalt promoted by thorium and magnesium in nine batches of catalyst 89; promoted nickel in two catalysts; promoted cobalt-nickel in five preparations.

In the group of cobalt–thorium–kieselguhr catalysts, 2A and 108B had the same percent composition, namely, cobalt : thoria (ThO_2) : kieselguhr : : 100 : 18 : 100 parts by weight, starting from the metal nitrates. Catalyst 12B, also obtained from the nitrate salts, was poorer in cobalt concentration and is described in terms of the oxides as follows: CoO : ThO_2 : kieselguhr : : 82 : 18 : 100 parts by weight. The cobalt–thorium–magnesium–kieselguhr preparations were different batches of the same catalyst—89A, B, H, I, J, K, L, N, and O. The constituents in this catalyst were present in the following ratio: Co : ThO_2 : MgO (magnesia) : kieselguhr : : 100 : 6 : 12 : 200 parts by weight. Catalysts 38A and 62A were nickel-promoted catalysts prepared in the laboratory of the International Nickel Fellowship at Mellon Institute for Bureau of Mines tests. Catalyst 38A was a manganese-promoted nickel preparation, with the following composition: NiO : MnO : $Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2$: : 83.2 : 16.8 : 100 parts by weight, starting from nickel nitrate, manganous sulfate, aluminum sulfate, and sodium aluminate. Catalyst 62A was precipitated on the carrier from nickel and thorium nitrates in the following ratio of constituents: NiO : ThO_2 : kieselguhr : : 91 : 9 : 100. The promoted cobalt–nickel catalysts contained equivalent ratios of the oxides of cobalt and nickel and, in addition, at least one other constituent and the carrier. This group of catalysts was prepared by the International Nickel Fellowship at Mellon Institute for Bureau of Mines tests. In three catalysts the additional constituent was thorium, giving CoO : NiO : ThO_2 : kieselguhr ratios as follows: 60A, 45.5 : 45.5 : 9 : 400 (type VIII Celite[9]); 61A, 45.5 : 45.5 : 9 : 100 (type III Celite); 64A, 46.36 : 46.36 : 4.6 : 100 (type VIII Celite), respectively. The composition of catalyst 65A was described as follows: CoO : NiO : ThO_2 : alumina pellets : : 20.1 : 20.1 : 4.0 : 100 parts by weight. Catalyst 36A, a manganese–aluminum-promoted preparation, precipitated on kieselguhr, had the following composition: CoO : NiO : MnO : Al_2O_3 : kieselguhr : : 40 : 40 : 16 : 4 : 100 parts by weight.

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[8] Work cited in footnote 98, p. 104.

[9] Johns-Manville trade name.

room temperature by potassium carbonate solution. The resulting gel was filtered, washed on the funnel, repulped into a slurry, again filtered, and again washed on the funnel. The precipitate was dried at 100° C. to give a yield of 117 percent, assuming complete dehydration of the oxides. The product as received in the Bureau of Mines laboratory was in the form of green, 10- to 50-mesh granules. The catalyst was powdered and pelleted in the usual manner.

EQUIPMENT USED IN PREPARING CATALYSTS

Most of the catalyst preparations described were laboratory batches; only 89H and 108B were made on a pilot-plant scale. Chemicals used in the laboratory-size preparations were weighed out on a metric torsion balance whose capacity was 4.5 kilograms and whose sensitivity was ⅕ gram. Precipitation in the laboratory was carried out in Pyrex battery jars of various dimensions, depending on the batch size. A ¼-pound batch was precipitated and washed by decantation in a 7-liter jar, 6 inches in diameter by 18 inches in height. Other sizes used were the 8¾ by 18 inches, of 14-liter capacity; 10⅜ by 18 inches, of 20-liter capacity; and 12 by 24 inches, of 40-liter capacity. Batches up to 4 pounds of finished catalyst were prepared in the 40-liter jars. The precipitated catalysts were filtered in Coors porcelain, two-piece Büchner-type funnels, with straight sides and permanent perforated filter plate. The funnels were of 2- and 3-gallon capacity.

Drying the catalysts at room temperatures up to 180° C. was accomplished in a laboratory electric drying oven. The over-all dimensions were 16½ inches wide by 16 inches deep by 25 inches high, and the inside dimensions 11 by 11 by 11 inches. Ovens were fitted with adjustable latticed metal shelves, with room for five plates.

Small batches of catalyst up to 5 pounds were compressed in a Stokes model "E" single-punch tablet machine. The pellet press had removable punches and dies, a single pulley with a speed of 80–100 r. p. m., and a ½-hp. motor. Pellets were manufactured at the rate of 90 tablets per minute and were ⅛ inch in diameter and ⅙ to ⅛ inch in length.

In the pilot-plant equipment chemicals were weighed on Fairbanks counter-type scales with a 300-pound capacity, 2-pound beam, and 0.01-pound sensitivity. The platform was 13½-inches square. Precipitation of batches larger than 5 pounds was carried out in a welded Monel tank mounted on four steel legs to a total height of about 50 inches. The tank had a diameter of 24 inches, a height of 30 inches, and a capacity of 60 gallons. The shape of the bottom was dished and in the center was a 1-inch-pipe-size outlet. The tank was fitted with a three-ring Monel steam coil for heating the contents of the vessel.

From the precipitation vessel the slurry was pumped into an 18-inch, four-eyed, closed-delivery, washing-type, cast-iron, 10-chamber filter press. The press had a flush plate and frame pattern with frames 1-inch thick, with a total capacity of 1.6 cubic feet. The pump was a turbine type, with a capacity on water of 11 gallons per minute at 20 feet head to 2 gallons per minute at 170 feet head. The filter cloths were were made of preshrunk cotton twill.

The filtered and washed catalyst was dropped on aluminum trays and dried in a steam-heated, circulating, hot-air drying closet. The cabinet was 8 feet 1 inch high and contained 16 galvanized welding wire-bottom trays which supported the aluminum plates whose dimensions were 35 by 28 inches open on the long sides.

An oscillating granulator crushed the soft cake through a 14- to 16-mesh wire screen by the oscillating motion of a set of rolls. The machine was of standard steel and cast iron. The powdered catalyst was then mixed with graphite in a granulating mixer constructed of steel and cast iron, and fitted with an inside spiral agitator. From the mixer the catalyst powder went to the pelleting machine. The large pellet press was a 33-punch rotary tablet machine. The press had a pulley with a speed of 380–760 r. p. m. and a 2-hp. motor. Pellets were manufactured at the rate of 1,000 tablets per minute and were ⅛ inch in diameter and 1/16 to ⅛ inch in length.