2. The solid–liquid equilibrium temperature and the heat of fusion have been determined. The melting point is 136.95°K. (−136.21°).

3. The vapor pressures have been determined from 200 to 289°K. and the results represented by an equation leading to a value for the normal boiling point and to values of the heat of vaporization at 230, 250 and 290°K. The normal boiling point is 10.84°.

4. The heat of vaporization has been determined at 273.25°K.

5. An assignment of the fundamental frequencies has been made, and the comparison between the calculated and observed entropies yielded a value of 1650 ± 400 cal./mole for the potential barrier hindering the internal rotation of the methyl group.

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Studies of the Fischer–Tropsch Synthesis. II. Properties of Unreduced Cobalt Catalysts[1, 1a]

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Introduction

Most of the successful cobalt Fischer–Tropsch catalysts are prepared by precipitation with sodium or potassium carbonate from an aqueous solution containing cobaltous nitrate and promoters such as thoria, magnesia or copper as nitrates.[4,5] In some catalysts magnesia in the form of a fine powder in an aqueous slurry is added at the time of precipitation.[6] Kieselguhr as a catalyst support is usually added at the time of precipitation, but it has been reported that catalysts of equal activity and life can be prepared by the addition of the kieselguhr to the moist precipitate.[7] Surface area and pore volume studies of Fischer–Tropsch catalysts have not been reported, but Ries[8] has described these properties of catalysts which may be inferred to be somewhat similar to Fischer–Tropsch catalysts. The nitrogen isotherms at −195° of his catalysts were "S"-shaped but showed a definite hysteresis on desorption. Their surface areas were many times greater than that of the kieselguhr used as a support. These catalysts were usually evacuated for sixteen hours at 340° before the isotherms or pore volumes were determined, so that the metal was probably present as oxide.

In this paper, surface area and pore volume studies are reported for two types of unreduced cobalt Fischer–Tropsch catalysts, and for similar preparations with promoters, kieselguhr or both omitted. The properties of the catalysts are compared and related to properties of the kieselguhrs that they contain. Precipitated catalysts of the cobalt–thoria–kieselguhr (100:18:100) type are designated by the number 108, and catalysts of the cobalt–thoria–magnesia–kieselguhr (100:6:12:200), prepared with finely divided magnesia, are designated by 89. Properties of the kieselguhrs used in these catalysts have been described by Anderson, McCartney, Hall and Hofer.[9] In later papers surface area and pore volume data of reduced cobalt Fischer–Tropsch catalysts and catalyst testing data will be reported.

Experimental

The preparation of the 89-catalysts has been described previously.[1a] A catalyst similar to these was 112A, which had the same ratio of cobalt–thoria–magnesia–kieselguhr, of 100:6:8:200, and the magnesia was precipitated from magnesium nitrate and added to the solution of cobalt and thorium nitrates. Since magnesium carbonate is fairly soluble, 20% more magnesium nitrate than the calculated amount was used. The 89- and 112-types with magnesia, thoria, kieselguhr or all three omitted were prepared in an identical manner, except for the omission of one or more of these components. The 108-catalysts were prepared in a similar manner to the 89-catalysts, with the magnesia omitted and potassium carbonate used as a precipitant instead of sodium carbonate.

Recently, Hall[10] communicated to us that the compositions of the magnesia-containing catalysts were uncertain because of the high solubility of magnesium oxide and carbonate. Analyses of the catalysts confirmed this, the ratios of cobalt:thoria:magnesia in the following catalysts being: 89H, 100:7.6:11.4; 89V, 100:8.3:10.3; 89Z, 100:7.0:8.5; 89BB, 100:6.3:12.1; 89EE, 100:6.1:12.5; and 112A, 100:6.2:8.1. The data indicate that, in many cases, the percentage of magnesia was lower than anticipated. Variation in the amount of thoria may be due to variable amounts of water of hydration in the salts used in preparing the catalysts. In the 108-catalysts the ratios of cobalt to thoria were near to those anticipated: 108B, 100:19.0; and 108E, 100:17.5.

Catalysts of the 89-series and similar preparations without promoters, kieselguhrs, or both were prepared in 150 to 300-g. batches, except catalysts 89H, 89CC, and 89-EE, which were made in 6.8-kg. batches. All 108-type catalysts were made in 13.6-kg. batches.

The catalysts were studied in the form of granules (G),

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[1a] Part I of this series, Anderson, Krieg, Seligman and O'Neill, see text *Ind. Eng. Chem.*, **39**, 1548 (1947).

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[4] Fisher and Koch, *Brennstoff-Chem.*, **13**, 61 (1932).

[5] Annual Reports of Fuels Research Board for Years Ending March 31, 1937, p. 136; 1938, p. 186; 1939, p. 151.

[6] Hall and Smith, *J. Soc. Chem. Ind.*, **65**, 128 (1946).

[7] Private communication from C. C. Hall. This effect is also described in captured German documents.

[8] Ries, Van Nordstrand, Johnson and Bauermeister, THIS JOURNAL, **67**, 1242 (1945).

[9] Anderson, McCartney, Hall and Hofer, submitted to *Ind. Eng. Chem.*, **39**, 1618 (1947).

[10] Private communication.

made by breaking the dried filter cake into 6- to 10-mesh pieces, and cylindrical pellets (P) of 1.6 mm. length and 3.2 mm. diameter, made from finely broken filter cake with 4% by weight of powdered graphite added as a die lubricant with Stokes, Model E, single-punch, and Model BB2, multiple-punch, pelleting machines. Larger pellets were made by pressing the finely broken filter cake into pellets (a process known as "slugging") which were then broken to form a high density powder that could satisfactorily be pressed into the larger pellets. In the preparation of 6.4 mm. length by 3.2 mm. diameter pellets (L. P.) of catalyst 108-B, small pellets (P) already prepared were crushed and repelleted; however, with catalyst 108-G large slugs of 12.7 mm. diameter by 3.2 mm. length were prepared and then crushed for repelleting. The latter is our usual procedure in preparing large pellets.

Nitrogen isotherms were determined by a volumetric method, as described by Emmett.[11] Surface areas were estimated by the use of the simple Brunauer, Emmett and Teller equation,[12] with the cross-sectional area of the adsorbed nitrogen molecule taken as 16.2 Å^2. Since the cobalt in the catalysts was in the form of a basic carbonate, it was desirable to evacuate the samples prior to study at a temperature at which the evacuation would minimize the effect of differences in drying the catalyst at the time of preparation. It was also desirable that the surface areas should not change on further treatment after a short period of evacuation. It was found that drying for one hour at 100°, followed by evacuation at 100° for one hour, was satisfactory. For example, surface areas of a sample of 89-Q, after drying at 100° and evacuating at room temperature, and after evacuating at 100° for one and two hours were 79.0, 85.7, 86.6 sq. m./g., respectively.

Pore volume studies were made by determining the densities by the displacement of helium and mercury on samples dried and evacuated at 100° as described above. Helium density measurements were made at 30° by the method of Smith and Rossman.[13] Mercury densities were determined by introducing mercury at an absolute pressure of 1140 mm. into evacuated samples. Under these conditions mercury should only penetrate pores larger than 5 microns.[14] The pore volume of the catalyst per gram (volume of pores not filled by mercury) is defined as the difference of the reciprocals of the mercury and helium densities. Void space per gram (volume filled by mercury) is defined as the difference of the reciprocals of the bulk and mercury densities.[15] For the pellets and granules of the catalysts described in this paper the void space is only the volume of the voids between particles, since it was found that particles of catalyst removed from the mercury without evacuation contained only very small amounts of mercury. Thus, it appears that most of the pores of the external surface of the catalyst were smaller than 5 microns in diameter, and the volume of the mercury displaced nearly equalled the external volume of the catalyst particle.

Experimental Results

Table I presents surface area and pore volume data of 89-catalysts and catalyst 112A in which the magnesia was precipitated from magnesium nitrate. Data for similar preparations without promoters, kieselguhr, or both, are given in Table II, and data for catalysts of the 108-type are given in Table III. Nitrogen isotherms at −195° of catalyst 89J in the granular and pelleted forms and of the kieselguhr used as a carrier are shown in Fig. 1. In Fig. 2 the specific mercury volumes of granular catalysts are plotted against the volume of mercury displaced by the weight of the respective kieselguhr in one gram of catalyst.

Surface Areas and Pore Diameters of Unreduced Catalysts

The surface areas of all of the precipitated catalysts (Tables I, II, and III) were many times greater than those of the kieselguhrs they contained. Catalysts of the 89-type, containing natural kieselguhr, had areas varying from 100 to 110 sq. m./g. in the granular form, and as pellets from 72 to 95 sq. m./g. (with the exception of 89O, 89CC and 89EE). Similar catalysts prepared with calcined and flux-calcined kieselguhrs had considerably lower areas; a granular catalyst of this type had an area of 84 sq.m./g, while the area of the pellets varied from 59 to 75 sq. m./g. This difference in area was larger than would be expected on an additive basis. There are two possible explanations of this: First, the fine structure of the natural kieselguhr may stabilize the cobalt basic carbonate–promoter complex[16] at the time of precipitation. Second, a fraction of the kieselguhr may dissolve and reprecipitate as silica gel in the precipitation process. The calcined kieselguhrs, being considerably less soluble, would undergo this process to a smaller extent. Other than this difference in areas, there appears to be no relationship between the areas of catalysts and of the kieselguhrs that they contain.

Three of the 89-catalysts, 89O, 89CC and 89EE, had anomalously high surface areas. The preparation of these catalysts was somewhat different from the rest of the series in that 89O contained alkali-washed magnesia, and there were possibly differences in the method of precipitation and drying; catalysts 89CC and 89EE were prepared in large batches (6.8 kg.) that were 30 times larger than the size of the other preparations. The surface areas of the 108-catalysts, all of which were prepared in large batches (13.6 kg.) showed variations from 72 to 125 sq. m./g.

Although a considerable fraction of the area of the kieselguhr was probably covered or blocked by the cobalt basic carbonate–promoter complex, the areas of this complex computed on an additive basis[16] were used to make comparisons with the areas of catalysts prepared without kieselguhr, promoters, or both. The areas of catalysts without kieselguhrs, which varied from 150 to 155 sq.

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(11) Emmett, "Advances in Colloid Science," edited by Kraemer, Vol. I, Interscience Publishers, New York, N. Y., 1942, pp. 1–36; Emmett, *Ind. Eng. Chem.*, **37**, 639 (1945).

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

(13) Smith and Rossman, *Ind. Eng. Chem.*, **35**, 972 (1943).

(14) Ritter and Drake, *Ind. Eng. Chem., Anal. Ed.*, **17**, 782 (1945).

(15) These definitions are not the same as those used in our paper on kieselguhrs[9] in which "pore volume" was termed "micropore volume" and "void space" was termed "macropore volume." The definitions used in the present paper are in agreement with current usage (see for example Brunauer, "The Adsorption of Gases and Vapors," Princeton University Press, Princeton, N. J., 1943, p. 376).

(16) Cobalt basic carbonate–promoter complex and cobalt complex are used synonymously in the remainder of the paper. The area of the complex is calculated assuming the areas of the kieselguhr and the complex to be additive, as shown in the following equations: $A_{\text{complex}} = A_{\text{catalyst}} - A_{\text{kg}}f_{\text{kg}}$. $A'_{\text{complex}} = A_{\text{complex}}/(1 - f_{\text{kg}})$ where A_{complex}, A_{catalyst} and A_{kg} are the surface areas of complex, catalyst and kieselguhr per gram, respectively, A'_{complex} is the area of complex per gram of complex, and f_{kg} is the weight fraction of kieselguhr in the catalyst.

TABLE I

PROPERTIES OF UNREDUCED COBALT–THORIA–MAGNESIA–KIESELGUHR (100:6:12:200) CATALYSTS

Catalyst	Form[a]	Co, %	Kieselguhr[b]	Surface areas, sq. m./g.			Densities, g./cc.		Pore vol.,[d] cc./g.	Average pore diameter,[e] Å.
				Kieselguhr	Catalyst	Complex[c]	Mercury	Helium		
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	0.511		1.60	766
	P	23.7	HSC	1.9	75.2	148.5	1.27		0.43	229
89J	G		F. C.	22.2	104.1	186.0	0.428	2.87	1.98	760
	P	24.5	F. C.	22.2	88.7	155.2	.974	2.76	0.66	297
89K	G		Port.	17.5	101.1	185.0	.611	2.77	1.28	506
	P	24.6	Port.	17.5	88.8	160.1	1.20	2.77	0.47	212
89L	P		HSC	1.9	58.6	115.2	1.34		.38	259
89N	P	24.8	HSC[f]	1.9	60.4	118.8				
89O	G		F. C.[g]	20.8	143.5	266.2				
	P	24.3	F. C.[g]	20.8	129.2	237.8	0.950		.69	213
89Q	P	23.8	Port.	17.5	85.7	156.0	1.10		.55	257
89U	G	23.4	Germ.	14.9	109.3	203.9	0.445		1.89	692
	P		Germ.	14.9	86.2	157.5	1.10	2.80	0.55	255
89V	G	24.3	D-911	29.3	101.9	174.5	0.544	2.82	1.50	589
	P		D-911	29.3	77.6	125.9	1.31		0.40	206
89Y	P		SA5	37.3	72.2	118.0	1.508		.30	165
89Z	P	24.7	658T	25.2	94.6	164.0	1.292	3.08	.41	173
89AA	P		JM II	5.5	61.7	118.0	1.480		.32	207
89BB	P	24.5	JM II	5.5	66.2	125.0	1.301	2.86	.40	242
89CC	P	24.5	F. C.	22.2	149.6	277.0				
89DD	P		S. F.	19.1	93.2	169.2	1.223		.46	198
89EE	G	24.7	F. C.	22.2	161.1	300.0	0.418	2.87	2.04	502
	P		F. C.	22.2	141.5	260.8	1.095	2.80	0.45	127
112A[h]	P	24.2	F. C.	22.2	78.0	133.8	1.052		.59	303

[a] G = granules, broken filter cake; P = pellets 1.6 mm. length by 3.2 mm. diameter. [b] Johns–Manville kieselguhrs: HSC = Hyflo Super Cel (flux calcined), JM II (calcined), F. C. = Filter Cel (natural), S. F. = Snowfloss (natural); Dicalite kieselguhrs: D-911 (natural), SA5 (natural), 658T (natural); Port. = Portuguese (natural); Germ. = German (natural). [c] Area of cobalt basic carbonate-promoter complex computed on an additive basis per gram of complex. See footnote 16. [d] The reciprocal of the mercury density minus the reciprocal of the helium density. Where helium density was not determined, it was assumed to be 2.80 for computation of pore volume. [e] Computed by the equation $\bar{d}$ = 4 × pore volume/surface area. [f] Acid-extracted, area probably unchanged. [g] Acid-extracted. [h] Contains precipitated magnesia.

TABLE II

PROPERTIES OF UNREDUCED CATALYSTS OF THE 89-TYPE WITH ONE OR MORE OF THE COMPONENTS OMITTED

(All preparations in the form of granules)[a]

Catalyst	Co, %	Kieselguhr[b]	Surface areas, sq. m./g.		Densities, g./cc.		Pore vol.,[d] cc./g.	Average pore diameter,[e] Å.
			Catalyst	Complex[c]	Mercury	Helium		
$Co:ThO_2:MgO$	48.9	None	149.0	149.0	0.676	3.80	1.22	327
(100:6:12)		None	154.8	154.8	.781	3.62	1.00	259
$Co:ThO_2$ (100:6)		None	171.0	171.0				
Co:MgO (100:12)	50.1	None	142.6	142.6				
Co:MgO[f] (100:8)	52.6	None	129.6	129.6				
Co:Kg		HSC	77.2	152.4				
(100:200)		F. C.	75.6	124.7	.457	2.71	1.75	926
Co (basic carbonate)		None	126.2	126.2	.925	3.81	0.82	293

[a] Granules, broken filter cake. [b] Johns–Manville kieselguhrs: HSC = Hyflo Super Cel (flux calcined), surface area = 1.9 sq. m./g.; F. C. = Filter Cel (natural), surface area 22.2 sq.m./g. [c] Area of the cobalt basic carbonate–promoter complex per gram of complex. See footnote 16. [d] Reciprocal of mercury density minus reciprocal of helium density. [e] Computed by the equation $\bar{d}$ = 4 × pore volume/surface area. [f] Contains precipitated magnesia.

m./g., were slightly less than the area of complex per gram of complex of granular 89I, which was prepared with flux-calcined kieselguhr, and considerably lower than the area of complex of catalysts prepared from natural kieselguhrs, which averaged 187 sq. m./g. of complex. Thus it appears that the presence of kieselguhr increased the area of the complex, calcined and flux-calcined kieselguhrs being very much less effective than natural kieselguhrs. The granular catalysts with

TABLE III

PROPERTIES OF UNREDUCED COBALT–THORIA–KIESELGUHR (100:18:100) CATALYSTS

Catalyst	Form[a]	Co, %	Kieselguhr[b]	Surface areas, sq. m./g. Kieselguhr	Catalyst	Complex[c]	Densities, g./cc. Mercury	Helium	Pore vol.,[d] cc./g.	Average pore diameter,[e] Å.
108B	G		F. C.	22.2	84.1	115.4	0.48		1.56	742
	P		F. C.	22.2	71.6	96.6	1.13	3.08	0.56	313
	LP	32.0	F. C.	22.2	66.5	89.0	1.51		.34	205
108B[f]	P		F. C.	22.2	77.2	105.0				
108G	VLP	34.0	F. C.	22.2	72.0	97.0	1.30	3.27	.46	257
108H	P	32.2	F. C.	22.2	125.0	170.0				
108I	P		F. C.	22.2	110.5	154.8				

[a] G = granules, broken filter cake; P = pellets, 1.6 mm. length by 3.2 mm. diameter; LP = pellets, 6.4 mm. length by 3.2 mm. diameter; VLP = pellets, 4.8 mm. length by 5.1 mm. diameter. [b] F. C. = Johns–Manville Filter Cel (natural). [c] Area of cobalt basic carbonate–promoter complex per gram of complex. See footnote 16. [d] The reciprocal of the mercury density minus the reciprocal of the helium density. [e] Computed by the equation $\bar{d} = 4 \times$ pore volume/surface area. [f] Without graphite.

kieselguhr but no promoters have areas somewhat smaller than those of the catalysts containing both promoters and kieselguhr. The area of the complex of a catalyst without promoters and kieselguhr was about 10% lower than that of the catalyst containing promoters but no kieselguhr. Catalyst 112A had a lower surface area than similar 89-catalysts. In cobalt–magnesia preparations it was also observed that the one containing precipitated magnesia had the lower surface area. Catalysts 108B and 108G have areas of the cobalt basic carbonate-thoria complex of the order of 100 sq. m./g., while the area of the complex for the 108H and 108I was about equal to those of 89-catalysts.

When granules were pelleted, the surface area decreased from 10 to 20%. For example, on pelleting into 1.6-mm.-length by 3.2-mm.-diameter cylinders, the area of catalyst 108B dropped from 84.1 to 71.6 sq. m./g., and when "slugged," broken into small pieces, and then repelleted into dense 6.4-mm.-length by 3.2-mm.-diameter cylin-

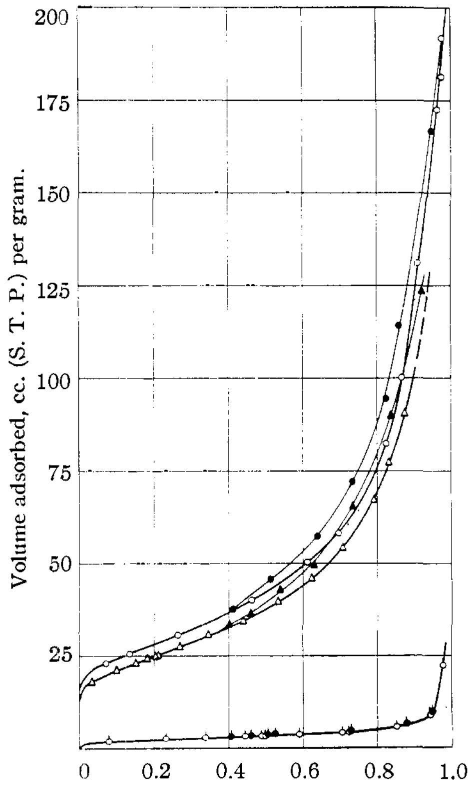

Fig. 1.—Adsorption isotherms of nitrogen at −195° of unreduced cobalt Fischer–Tropsch catalyst 89J in granular and pelleted forms and the kieselguhr used as a catalyst support plotted for the weight of kieselguhr per gram of catalyst: o, represents 89J granules, Δ, represents 89J pellets, and ȯ, the kieselguhr. Adsorption points are open and desorption points are solid.

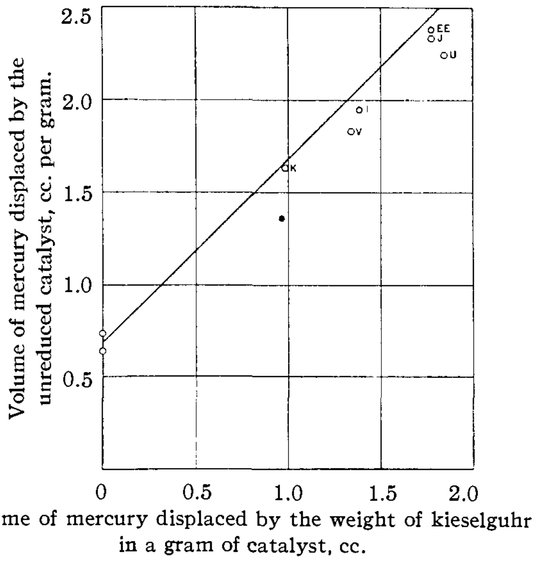

Fig. 2.—The volumes of mercury displaced per gram of unreduced cobalt Fischer–Tropsch catalysts of the 89-type in granular form plotted against the volume of mercury displaced by the weight of kieselguhr per gram of catalyst. The mercury displacement experiments were made at an absolute pressure of 1140 mm. The line represents a hypothetical additive relationship between the volumes of mercury displaced by the catalyst and by the kieselguhr.

ders, the area dropped to 66.5 sq. m./g. This decrease in area may be due to several causes, two of which will be discussed briefly. First, the graphite used as a die lubricant formed highly polished external surfaces on the pellets, and it has been suggested that the graphite on the external surface and within the pellet may block the entrance to closed-end pores. To test this, 1.6-mm.-length by 3.2-mm.-diameter pellets of 108B were made without graphite. The resistance of this material to pelleting was sufficient to stop the motor of the pelleting machine and necessitated operation by hand. The pellets made in this manner were soft and poorly formed. Their area decreased to 77.2 sq. m./g., which was greater than that for pellets containing graphite; however, the greater area may be due to the fact that these pellets were poorly formed and not compressed as much as those containing graphite. With this catalyst the decrease in area was due to factors other than pore blocking by graphite, even though pore blocking in catalysts containing graphite cannot be excluded on the basis of this experiment. The second and more plausible explanation is that some of the particles of the cobalt basic carbonate–promoter complex were pressed together so closely that nitrogen molecules could not penetrate the spaces between them. In pelleting, considerable deformation of the catalyst occurred, since the volume occupied by a pelleted catalyst is a half to a third of the bulk volume of the kieselguhr it contains.

The nitrogen adsorption isotherms at −195° of precipitated cobalt catalysts were of Type II of Brunauer's classification[8,17] with hysteresis as shown for granular and pelleted 89J in Fig. 1. Included in this figure is the isotherm for the kieselguhr used as a support plotted for the weight of kieselguhr per gram of catalyst. From the isotherms the majority of the pores of the catalyst may be estimated to be larger than 100 Å. in diameter, with some smaller pores which give the hysteresis in the 0.4 to 0.7 relative pressure region. Figure 1 shows that the hysteresis observed in the isotherms of the catalysts is not the hysteresis of the kieselguhr contained in the catalyst.[9] The value of k as defined in the modified B.E.T. equation of Anderson[18] was 0.85 compared with 0.7 usually observed for non-porous materials. It will be shown in a later paper that values of k higher than 0.7 are usually indicative of systems containing some small pores with diameters of 100 Å. or less.

The average pore diameter may be estimated from the ratio of pore volume to surface area with the equation for cylindrical pores, $\bar{d} = 4 \times$ pore volume/surface area.[19,20] These average pore diameters of granular catalysts varied from 500 to 770 Å., while those for pelleted catalysts varied from 165 to 310 Å. The pore diameters of both granular and pelleted catalysts, 108B and G, were larger than for most other catalysts, reflecting their low surface areas. The average pore diameters of catalysts prepared without promoters were slightly larger, and those of preparations without kieselguhrs were considerably smaller than the average pore diameters of the granular 89 catalysts.

Relationship between Pore Volumes of Catalysts and Kieselguhrs

As mentioned in the previous section, no relationship exists between the surface areas of the catalysts and their respective kieselguhrs except that the catalysts containing natural kieselguhrs have higher areas than those with calcined kieselguhr. However, correlations were found between the pore volumes of granular catalysts and kieselguhrs. The specific mercury volume of the granular catalyst was roughly equal to the bulk volume of the kieselguhr it contained. The data also indicate that most of the cobalt basic carbonate–promoter complex was precipitated in the void space of the kieselguhr and that only a small amount entered the pore volume. This is shown in Fig. 2, in which the volume of mercury displaced by a gram of catalyst is plotted against the volume of mercury displaced by the weight of kieselguhr contained in one gram of catalyst. The points fall only slightly below the hypothetical line of the sum of the mercury displaced by the cobalt basic carbonate–promoter complex plus the mercury displaced by the kieselguhr, indicating that most of the cobalt promoter complex was deposited in the void space of the kieselguhr. In most cases the void space of the kieselguhr was sufficiently large to hold all of the complex, and the specific mercury volumes of these catalysts were somewhat less than the bulk volume of the kieselguhr that it contained. With granular catalyst 89K the void space of the kieselguhr was less than the volume of the cobalt complex, and in this case the specific mercury volume of the catalyst was greater than the bulk volume of the kieselguhr.

Pelleting was difficult to perform reproducibly, and little correlation was found between pelleted catalysts and kieselguhrs. The external volume of the pellets was usually about one-third of the bulk volume of the kieselguhr it contained. The pore volumes of the pelleted catalysts were very much smaller than those of the kieselguhr, indi-

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(17) Brunauer, Deming, Deming and Teller, THIS JOURNAL, **62**, 1723 (1940); Brunauer, "The Adsorption of Gases and Vapors," Princeton University Press, Princeton, N. J., 1943, p. 150.

(18) Anderson, THIS JOURNAL, **68**, 686 (1946).

(19) Emmett and DeWitt, *ibid.*, **65**, 1253 (1943); see also ref. 8.

(20) These average pore diameters are by definition $\bar{d} = \Sigma d^2 l/\Sigma dl$ where l is the length of a capillary of diameter d. The mean diameter $\bar{d}$ is equal to the arithmetic mean $d_A = \Sigma dl/\Sigma l$, only in the case in which all pores have the same diameter. In all other cases $\bar{d}$ is greater than d_A as given by the relationship $\bar{d} = d_A + \sigma^2/d_A$ where σ is the standard deviation of the pore distribution. In the case of the catalysts discussed in this paper, the pores of the complex average about 300 Å. and the pores of the kieselguhr about 5000 Å.; hence, $\bar{d}$ is considerably larger than d_A.

cating that the void space of the kieselguhr was decreased in pelleting and probably a large quantity of the cobalt complex was forced into pore volume of the kieselguhr.

Discussion

The data presented show that catalysts may be prepared with fairly reproducible surface areas in small batches, but in large preparations considerable variation occurred. This is believed to be due to difficulty in controlling time and conditions of precipitation, washing and drying. Most of the area of the catalyst was due to the cobalt basic carbonate--promoter complex, the additive contribution of the kieselguhr being less than 20% of the total area in every case. The promoters do not contribute very much to the surface area of the unreduced catalyst. The adsorption isotherms of nitrogen at −195° resembled those reported by Ries,[8] except that the hysteresis was less pronounced with the catalysts described here. Ries also reported that the surface areas were equal in granular and pelleted forms. Both of these differences may arise from the fact that the catalysts of Ries were evacuated at high temperatures (350°) for extended periods before use. This treatment would probably remove most of the water and carbon dioxide in the catalyst, thus possibly enlarging the spaces between particles and forming additional pores.

The following picture of the granular catalysts containing kieselguhr was formulated from the data presented. The kieselguhr acts as a "brush-pile," the smaller particles of cobalt basic carbonate-promoter complex being precipitated into the void space volume of the kieselguhr without appreciably changing its bulk volume. Apparently, only a small fraction of the complex enters the pore volume of the kieselguhr. This may explain why catalysts of equal activity and life could be prepared by adding the kieselguhr either during or after the precipitation. If a major part of the cobalt complex is deposited within the pore volume of the kieselguhr when precipitation occurs in the presence of kieselguhr, it is probable that the time of the addition of kieselguhr would change the activity and life of the catalyst. On pelleting rather drastic changes occur. The volume of the catalyst is reduced to one-half to one-third of its volume as granules. The volume of the pellets is less than the bulk volume of the kieselguhr it contains, which indicates that the pore volume and void space of the kieselguhr are decreased. Possibly the cobalt complex is forced into the pore volume of the kieselguhr. The granular catalysts containing kieselguhr have average pore diameters which are about three times larger than those of similar preparations without kieselguhr. This is probably due to averaging the larger pore diameters of the pore volume of the kieselguhr with the smaller pore diameter of the cobalt complex.

Recently, Ries[21] reported studies of the adsorption of nitrogen at −195° and stearic acid from solution on catalysts similar to those described in his previous papers. All of his catalysts were calcined for two hours at 350° before the adsorption determinations. His catalyst prepared with the kieselguhr support formed a small pore structure with high area, while the other catalysts formed finely divided, relatively non-porous particles with lower surface areas. In view of the present work, it appears that the areas of the catalysts of Ries were probably about equal after precipitation and drying but changed during the calcination. Processes of crystal growth and contraction in bulk volume probably are greatly inhibited by the kieselguhr support, which defines the bulk volume of the catalyst.

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Summary

1. The areas of unreduced precipitated cobalt Fischer–Tropsch catalysts were several times greater than those of the kieselguhr used as carriers. Catalysts prepared with natural kieselguhrs had larger areas than those prepared with calcined or flux calcined kieselguhrs. Areas of unreduced catalysts varied from 60 to 150 sq. m./g.

2. Average pore diameters of granular catalysts varied from 500 to 770 Å. and for pelleted catalysts from 165 to 310 Å. The surface areas of pelleted catalysts were 10 to 20% lower than the areas of the corresponding granules.

3. It was shown that the cobalt basic carbonate–promoter complex was precipitated chiefly in the void space of the kieselguhr.

4. Preparations without promoters, kieselguhr or both had areas of the cobalt complex per gram of complex that were roughly equal to the area of the complex of the catalyst. Natural kieselguhr as a carrier considerably increased the area of the cobalt complex.

5. Catalysts prepared in small batches were quite reproducible with respect to surface area, but the areas of catalysts prepared in large batches varied considerably.

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[21] Ries, *J. Chem. Phys.*, **14**, 465 (1946).