

[CONTRIBUTION FROM THE CENTRAL EXPERIMENT STATION, BUREAU OF MINES]

Studies of the Fischer-Tropsch Synthesis. IV. Properties of Reduced Cobalt Catalysts¹

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A number of catalysts of easily reducible metals are prepared by precipitation of their oxides or carbonates, followed by reduction in hydrogen to the metal. Since most precipitated oxides or carbonates sinter excessively on reduction, with decreases in both surface area and bulk volume, promoters and carriers are added to minimize these effects. This paper describes such changes for cobalt-thoria-kieselguhr and cobalt-thoria-magnesia-kieselguhr Fischer-Tropsch catalysts and similar preparations with one or more of the components omitted. Also included are carbon monoxide chemisorption and X-ray diffraction studies.

Properties of these catalysts in the unreduced state³ and of the kieselguhrs used as carriers,⁴ and the characteristics of these catalysts in the synthesis^{5,6} have been reported previously. It was shown that the surface areas of the cobalt-basic carbonate-promoter complex⁷ were only slightly increased by additions of promoters and, or, carriers. However the kieselguhr increased the bulk volume of the catalyst; the bulk volume of granular catalysts containing kieselguhr varied directly with the bulk volume of the kieselguhr. It was also shown that the cobalt basic carbonate was deposited chiefly in the pores of the kieselguhr that were larger than 5 microns in diameter.

Hofer and Peebles^{8,9} have reported X-ray diffraction studies of some of this series of catalysts after reduction, carburization and use in the synthesis. McCartney and Anderson¹⁰ have reported electron micrograph and adsorption studies of changes of a pure cobalt oxide powder upon reduction. In a subsequent section of this paper, the results are compared with those of Emmett

and Brunauer¹¹ on reduced iron synthetic ammonia catalysts. Surface-area studies of iron Fischer-Tropsch catalysts, now in progress, will be reported in a later paper.

Experimental

The catalysts studied were cobalt-thoria-kieselguhr (100:18:100) catalyst designated by 108B, a series of cobalt-thoria-magnesia-kieselguhr (100:6:12:200) designated as 89 and preparations similar to the 89-series with one or more components omitted. The methods of preparing these catalysts have been reported in previous papers.^{3,5,12} Hofer and Peebles⁸ have described the preparation of the cobalt oxide powder used in this work. For reduction, adsorption and density studies, the catalysts were placed in an adsorption vessel with a special four-way stopcock which permitted hydrogen to be flowed over the catalyst during reduction.¹³ To facilitate filling and removal of catalysts without change in volume of the vessel, the charge tube as shown previously was extended to the level of the stopcock and closed with a ground-glass joint. After filling of the adsorption vessel a close-fitting glass rod was inserted into the charge tube to minimize the dead space. Adsorption and reduction studies were made in a small vessel which held about one gram of catalyst, and density determinations were made in a larger vessel holding about ten grams. Helium and mercury densities were made on the same reduced sample. In all cases, the reduced catalysts were handled in a manner which precluded exposure to air.

The hydrogen for the reduction was passed over hot copper and through anhydrous magnesium perchlorate to remove traces of oxygen and water vapor. The adsorption vessel was heated in a horizontal position to avoid heating the stopcock and ground joint. The small resistance furnace used to heat the samples was controlled automatically to $\pm 3^\circ$.

Before reduction the samples were evacuated at 100° for one hour to remove adsorbed vapors and to minimize the effect of differences in drying of the samples. The weights of samples after this treatment were used in computing surface areas, and except for the data in Table III the areas of reduced catalysts were expressed per gram of unreduced catalyst. The reduction procedure was to heat the catalyst rapidly to reduction temperature, 360 or 400° , in a slow stream of nitrogen. Since the cobalt was present as a basic carbonate, about 65% of the total weight loss on reduction occurred during this treatment. When the reduction temperature was reached, hydrogen at a space velocity¹⁴ of 6000 was passed over the catalyst for two hours. Then the catalyst was evacuated at the reduction temperature to a vacuum of less than 10^{-3} mm. to remove chemisorbed hydrogen.

Adsorption isotherms were determined by conventional volumetric methods.¹⁵ The gases used were of high purity, containing considerably less than 0.1% of oxygen. Before starting the carbon monoxide isotherms, the samples were

(1) Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior. Not copyrighted.

(2) Physical Chemists, Bureau of Mines, Central Experiment Station, Pittsburgh, Pa.

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

(4) Anderson, McCartney, Hall and Hofer, *Ind. Eng. Chem.*, **39**, 1618 (1947).

(5) Anderson, Krieg, Seligman and O'Neill, *ibid.*, **39**, 1548 (1947).

(6) Anderson, Krieg, Seligman and Tarn, *ibid.*, in press.

(7) The area of the cobalt-promoter complex was calculated with the following equations which assume the area of kieselguhr to be additive, $A_{\text{complex}} = A_{\text{catalyst}} - f_{\text{KG}}A_{\text{KG}}$, where A_{complex} , A_{catalyst} and A_{KG} are the area of the complex and catalyst per gram of unreduced catalyst and the area of kieselguhr per gram respectively and f_{KG} is the weight fraction of kieselguhr in the unreduced catalyst. The area of complex per gram of complex in the unreduced catalyst was obtained by dividing A_{complex} by $1 - f_{\text{KG}}$. It should be mentioned that the area of the kieselguhr did not change appreciably when subjected to the usual reduction procedures.

(8) Hofer and Peebles, *THIS JOURNAL*, **69**, 893 (1947).

(9) Hofer and Peebles, *ibid.*, **69**, 2497 (1947).

(10) McCartney and Anderson, *J. Appl. Phys.*, **18**, 902 (1947).

(11) This work is summarized in Brunauer and Emmett, *THIS JOURNAL*, **62**, 1733 (1940).

(12) Storch, *et al.*, Bureau of Mines Technical Paper 709; Synthetic Liquid Fuels Process. Hydrogenation of carbon monoxide. Part I, in press.

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

(14) Volumes of hydrogen (S. T. P.) per volume of catalyst space per hour.

(15) Emmett, "Advances in Colloid Science," ed. by Kraemer, Vol. I, Interscience Publishers, New York, N. Y., 1942, pp. 1-36.

TABLE I
SURFACE AREAS OF UNREDUCED AND REDUCED COBALT FISCHER-TROPSCH CATALYSTS

Catalyst	Form ^a	Kiesel- ^b guhr	Method of reduction ^c			Surface areas of catalysts, sq. m.				Ratio of area of complex after to before reduction
			Temp., °C.	Hours	% Wt. loss	Unreduced		Reduced		
						Total per gram	Complex per gram of complex	Total ^d per gram	Complex ^e per gram of complex	
Co:ThO ₂ :MgO:Kg = 100:6:12:200										
89H	P	H. S. C.	400	2	19.8	67.2	127.2	41.9	83.8	0.620
89J	P	F. C.	400	2	17.4	85.5	155.4	62.0	99.6	.640
89K	P	Port.	400	2	19.7	88.8	160.3	62.7	105.5	.651
89K	G	Port.	400	2	17.7	101.1	185.0	62.2	104.5	.580
89U	P	Germ.	400	2	19.3	86.2	157.5	37.8	59.6	.374
89V	P	D-911	400	2	20.4	77.6	126.0	50.2	70.1	.550
89BB	P	JM-II	400	2	18.9	66.2	121.5	46.2	84.6	.690
89FF	P	FCX	400	2	16.7	102.9	177.5	80.2	133.2	.751
Co:ThO ₂ :KG = 100:18:100										
108B	P	F. C.	360	2	24.4	71.6	96.2	32.4	50.0	.390
Co:ThO ₂ :MgO = 100:6:12										
	G	None	400	2	37.7	154.8	154.8	52.8	52.8	.341
Co:ThO ₂ = 100:6										
	G	None	400	2	38.7	171.0	171.0	14.6	14.6	.085
Co:MgO ^f = 100:12										
	G	None	400	2	41.6	142.6	142.6	35.2	35.2	.247
Co:MgO ^g = 100:8										
	G	None	400	2	42.0	129.6	129.6	18.3	18.3	.141
Co:Kg = 100:200										
	G	F. C.	400	2	21.1	75.6	124.7	18.3	14.2	.109
Co:Kg = 100:200										
	G	H. S. C.	400	2	21.2	77.2	152.4	6.87	12.0	.078
Cobalt basic carbonate										
	G	None	400	2	44.2	126.2	126.2	2.5	2.5	.020
Cobalt oxide powder										
	^h	None	250	24	30.2	67.0	67.0	3.2	3.2	.048

^a G = granules, broken filter cake; P = pellets (1.6 mm. long by 3.2 mm. diameter). ^b H. S. C. = Johns Manville Hyflo Super-Cel, F. C. = Johns Manville Filter-Cel, Port. = Portuguese kieselguhr, D-911 = Dicalite 911, JM-II = Johns Manville II, FCX = acid extracted Filter-Cel. For a complete description of these samples see references 4 and 6. ^c All reductions except cobalt oxide powder were made with hydrogen at space velocities per hour of 6000. Cobalt oxide powder was reduced in hydrogen at a space velocity of 100. ^d Per gram of unreduced catalyst. ^e Per gram of complex in unreduced catalyst. ^f Contains powdered magnesia. ^g Contains precipitated magnesia. ^h A fine powder.

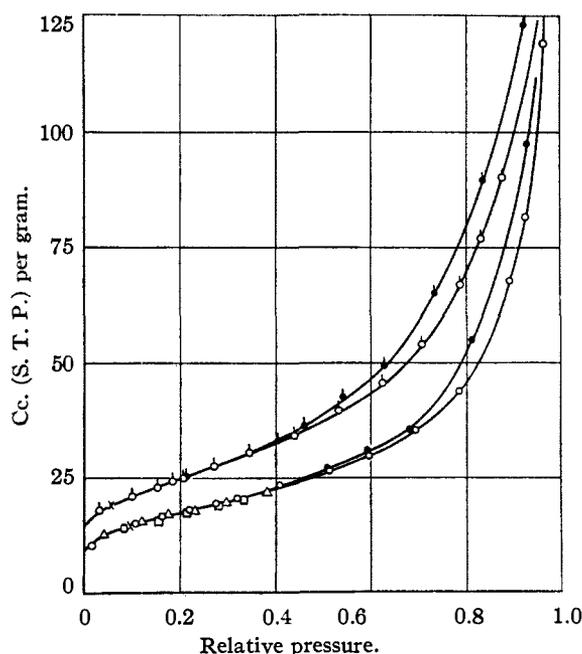


Fig. 1.—Adsorption of nitrogen at -195° on unreduced and reduced cobalt catalyst 89J, where \circ represents the unreduced catalyst and \square , \triangle and \bullet represent different samples of reduced catalyst. Desorption points are solid, and the volume of gas corresponding to a monolayer is represented by X.

cooled in helium at -195° to ensure temperature equilibration. Surface areas were computed from the simple B. E. T. equation¹⁶ with the cross-sectional area of the nitrogen molecule taken as 16.2 sq. Å. The methods of determining helium and mercury densities have been described previously.^{3,4}

The samples used in X-ray diffraction analysis were reduced, using the same conditions as those above. They were opened under petroleum ether and stored for a few days under this liquid. The samples, wet with petroleum ether, were ground to a paste, mixed with collodion and partly extruded from a section of stainless steel tubing. This technique is described by Barrett.¹⁷ The tubing was 19 gage 0.7 mm. inside diameter. The specimens were mounted in a Debye-Scherrer powder camera of 71.62 mm. inside diameter. FeK_{α} radiation from a sealed-off X-ray tube equipped with beryllium windows with manganese dioxide filters was used. The tube was operated at 30 kv. and 7 ma.

Experimental Results

Surface-area data for unreduced and reduced catalysts and similar preparations are given in Table I. Also included are areas for the cobalt-promoter complex⁷ computed by assuming the area of the kieselguhr to be additive. Since part of the surface area of the kieselguhr may be covered or blocked by the cobalt-promoter complex, this area of complex must be considered as the lower limit of its actual value. Nitrogen isotherms at -195° of pelleted catalyst 89J before and after reduction are given in Fig. 1.

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

(17) Barrett, "Structure of Metals," McGraw-Hill Book Co., Inc., New York, N. Y., 1943, p. 118.

TABLE II
CHANGES IN SURFACE AREA DURING HEATING AND REDUCTION
(All data per gram of original unreduced catalyst or complex)

Catalyst	Original catalyst		Heated catalyst ^a		Evacuated catalyst ^a		Reduced catalyst ^a	
	Area sq. m./g.	Area of complex per gram complex	Area sq. m./g.	Area of complex per gram complex	Area sq. m./g.	Area of complex per gram complex	Area sq. m./g.	Area of complex per gram complex
Co:ThO ₂ :MgO:KG = 100:6:12:200, 89J	85.5	155.4	65.5	108.9	67.0	109.8	62.0	99.6
Co:ThO ₂ :MgO = 100:6:12	154.8	154.8	68.3	68.3	61.1	61.1	52.8	52.8
Co:Kg ^b = 100:200	75.6	124.7	37.1	52.4	35.5	49.2	18.3	14.2
Cobalt basic carbonate	126.2	126.2	24.2	24.2	21.6	21.6	2.5	2.5

^a Area of catalyst and complex per gram of catalyst and per gram of complex in the original unreduced catalyst respectively. ^b Contains Filter-Cel.

TABLE III
MERCURY AND HELIUM DENSITIES OF UNREDUCED AND REDUCED COBALT CATALYSTS

Catalyst	Form ^a	Unreduced catalysts					Reduced catalysts					Mercury volumes per gram of un- reduced catalyst, cc.	
		Densities Hg	He	Pore volume cc./g.	Area sq. m./g.	\bar{d} , ^b Å.	Densities Hg	He ^c	Pore ^d volume cc./g.	Area ^d sq. m./g.	\bar{d} , ^b Å.	Before reduc- tion	After reduc- tion
Co:ThO ₂ :MgO:KG = 100:6:12:200													
89H	P	1.20	2.74	0.47	67.2	280	0.993	3.10	0.68	51.8	527	0.833	0.816
89J	P	0.974	2.76	0.66	88.7	297	0.780	3.07	0.95	76.6	500	1.026	1.037
89K	P	1.20	2.77	0.47	88.8	212	1.045	3.08	0.63	77.4	327	0.833	0.768
89K	G	0.611	2.77	1.28	101.1	506	0.537	3.13	1.54	76.8	804	1.635	1.530
89U	P	1.10	2.80	0.55	86.2	255	0.901	3.08	0.79	46.7	672	0.909	0.896
89FF	P	1.295	*	0.41	102.9	160	1.138	3.03	0.55	99.0	222	0.772	0.712
Co:ThO ₂ :KG = 100:18:100													
108B	P	1.13	3.08	0.56	71.6	313	0.905	3.69	0.73	42.3	693	0.885	0.836
Co:ThO ₂ :MgO =													
100:6:12	G	0.781	3.62	1.00	154.8	259	1.057	6.72	0.80	84.1	379	1.280	0.593
Co:KG = 100:200	G	0.457	2.71	1.75	75.6	926	0.378	3.00	2.31	22.8	4060	2.189	2.082
Cobalt basic carbonate	G	0.925	3.81	0.82	126.1	293	4.476 ^f	9.00	0.112	4.2	1070	1.081	0.125

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

TABLE IV
CHEMISORPTION OF CARBON MONOXIDE ON REDUCED COBALT FISCHER-TROPSCH CATALYSTS
All data per gram of unreduced catalyst

Catalyst	Form ^a	V _m cc.	V _{CO} , ^b cc.	Complex per gram of complex		V _{CO} cc.	V _{CO} V _{m-complex}	Co atoms ^c in surface, %
				V _m , cc.	V _{CO} , cc.			
Co:ThO ₂ :MgO:KG = 100:6:12:200	P	9.58	4.40	18.72	8.80	0.470	72.3	
89J	P	14.15	3.10	23.92	6.20	.259	39.9	
89K	P	14.31	3.80	24.80	7.60	.306	47.1	
89K	G	14.19	4.00	24.40	8.00	.328	50.4	
89U	P	8.64	2.17	13.98	4.34	.311	47.9	
89V	P	11.48	3.80	16.48	7.60	.461	71.0	
Co:ThO ₂ :KG = 100:18:100								
108B	P	7.40	2.56	11.42	2.84	.448	69.0	
Co:ThO ₂ :MgO = 100:6:12	G	12.06	6.90	12.06	6.90	.572	88.0	
Co:ThO ₂ = 100:6	G	3.33	1.95	3.33	1.95	.586	90.2	
Co:MgO ^d = 100:12	G	8.03	3.70	8.03	3.70	.461	71.0	
Co:MgO ^e = 100:8	G	4.17	2.17	4.17	2.17	.520	80.0	
Co:KG ^f = 100:200	G	4.18	0.85	3.28	1.70	.518	79.7	
Cobalt basic carbonate	G	0.58	0.36	0.58	0.36	.632	97.2	
Cobalt oxide powder		0.73	0.73	0.48	0.48	.648	99.7	

^a G = granules, broken filter cake; P = pellets. ^b V_{CO} computed from the difference the total carbon monoxide isotherms and the physical nitrogen at equal relative pressures. ^c V_{CO}/V_{m-complex} divided by 0.65, the value of V_{CO}/V_{m-complex} for cobalt metal. ^d Powdered magnesia. ^e Precipitated magnesia. ^f Filter-Cel.

Data for changes in surface area during a one-hour treatment with nitrogen at 400° and in a subsequent evacuation at 400° for sixteen hours are presented in Table II. Data for helium and mercury densities (the latter determined at 1 atmosphere), pore volumes,¹⁸ and average pore diameters, \bar{d} , computed from the equation for open end cylindrical pores¹⁹ $\bar{d} = 4V/A$, where V is the pore volume and A the surface area, are given in Table III. In Table IV data for the chemisorption of carbon monoxide are presented and compared with the volume of nitrogen required to form a physical monolayer. In Fig. 2 are typical carbon monoxide and nitrogen isotherms at -195° for reduced catalysts. In Table V are given X-ray diffraction data for catalysts and similar preparations.

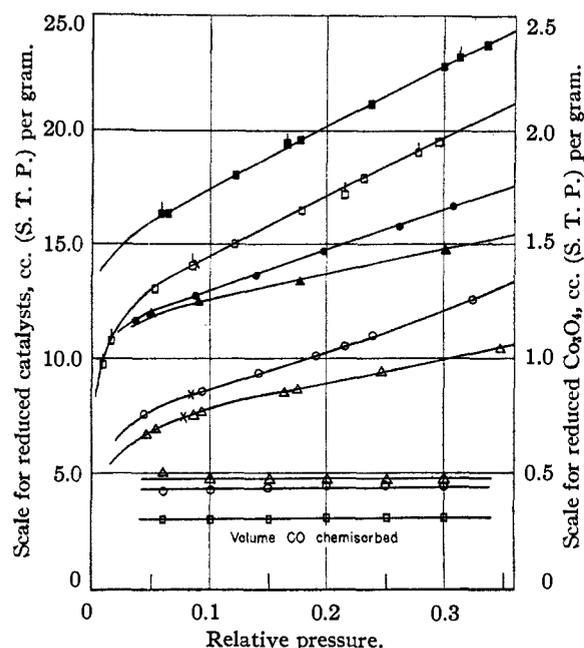


Fig. 2.—Sorption of nitrogen and carbon monoxide at -195° on reduced pelleted catalysts 89H and 89J and reduced cobalt oxide powder where open points represent nitrogen and solid points represent carbon monoxide isotherms. Points of reduced 89H are given by O, two samples of reduced 89J by □ and ◻, and the reduced cobalt oxide by Δ. The volumes of chemisorbed carbon monoxide are given in lower part of the graph.

Changes of Surface Area on Reduction

In Fig. 1 the circles, squares and triangles of the isotherm of the reduced catalyst indicate the reproducibility of isotherms of three different reductions of pelleted catalyst 89J. Isotherms of both unreduced and reduced catalysts showed hysteresis at relative pressures greater than 0.4. The hy-

(18) The volume of pores with openings smaller than 5 microns in diameter (pores not filled by mercury at atmospheric pressure) computed from the difference of the reciprocals of the mercury and helium densities.

(19) Emmett and DeWitt, *THIS JOURNAL*, **65**, 1253 (1943).

TABLE V
X-RAY DIFFRACTION DATA

Preparation	Dif-fuse-ness ^a	X-Ray reflections				
		Face-centered cubic		Hexagonal close-packed		
		hkl	d/n, Å. ^b	I	hkl	d/n, Å.
Cobalt basic carbonate (unsupported)	B	S 111	2.04	w	10 $\bar{1}$ 0	2.15
		M 200	1.76	w	10 $\bar{1}$ 1	1.91
		S 220	1.25			
		S 311	1.06			
Cobalt basic carbonate (on Filter Cel)	C	vS 111	2.04	w	10 $\bar{1}$ 0	2.14
		M 220	1.25			
		M 311	1.06			
Co: ThO ₂ (100:6) (unsupported)	C	S 111	2.04	w	10 $\bar{1}$ 0	2.15
		M 220	1.25			
		M 311	1.06			
Co: MgO (100:8) (unsupported)	C	vS 111	2.02			
		w 200	1.76			
		M 220	1.25			
		S 311	1.06			
Co: MgO (100:12) (unsupported)	D	vS 111	2.02			
		w 200	1.77			
		M 220	1.25			
		M 311	1.06			
Co: MgO: ThO ₂ (100:12:6) (unsupported)	D	M 111	2.02			
		vw 200	1.76			
		w 220	1.24			
		w 311	1.06			
89J Co: ThO: MgO: Filter Cel (100:6:12:200)	D	M 111	2.02			
		w 220	1.25			
		w 311	1.06			
89H Co: ThO ₂ : MgO: Hyflo Super-Cel (100:6:12:200)	D	M 111	2.00			
		w 220	1.24			
		w 311	1.06			
108B Co: ThO ₂ : Filter-Cel (100:18:100)	D	M 111	2.04			
		M 220	1.25			
		M 311	1.06			

^a B = diffuse; C = more diffuse; D = very diffuse.
^b vS = very strong; S = strong; M = medium; w = weak; vw = very weak.

steresis loop in the range of relative pressures of 0.4 to 0.7 was considerably smaller for the reduced catalyst than for the unreduced, the hysteresis of the isotherm of the reduced catalyst being only slightly greater than that of the isotherm of the kieselguhr that it contained. This may indicate enlargement or removal of some of the pores of diameters less than 50 Å., since hysteresis in this range is usually related to the presence of small pores.

The data in Table I show that the surface areas of all of the catalysts studied decreased on reduction. The areas of the cobalt-promoter complex⁷ of the catalysts containing both promoters and carriers decreased to 37.4 to 75% of the area of the complex of the unreduced catalysts. The area of catalysts with promoter but no kieselguhr decreased to 8.5 to 34.1% of the unreduced areas. The areas of the complex of preparations containing kieselguhr but no promoters decreased to 7.8 to 10.9% of the unreduced areas, and the area of the preparation with neither promoter nor carriers decreased to 2.0% of the unreduced area. Thus it is observed that catalysts of the 89 type were most resistant to sintering upon reduction. Catalysts with calcined and flux-calcined kieselguhrs, 89BB and 89H, respectively, did not sinter any more

than catalysts prepared from natural kieselguhrs. However, since the areas of these catalysts in the unreduced state were less than those of catalysts with the natural kieselguhrs, the areas of reduced catalysts 89H and BB were less than the rest of the 89 series. Of the individual promoters, magnesia added as a powder appears to be the most effective and thoria the least. However, the data for the preparations with powdered magnesia may be misleading, since the magnesia itself has a high area which is probably not appreciably decreased in the preparation or reduction²⁰ and thus may increase the total area. Consistent with this, the volume of chemisorbed carbon monoxide per unit surface area (Table IV) was less for preparations with powdered magnesia than for the other samples. Thoria was not very effective in preventing sintering in either the cobalt-thoria preparation or in catalyst 108B. Kieselguhr appears to be nearly as effective as the thoria, the natural kieselguhrs being only slightly more effective than flux-calcined Hyflo Super-Cel.

The surface areas of unreduced catalysts³ as granules (broken filter cake) was 10 to 15% greater than those of corresponding pelleted catalysts. Here, the explanation was given that the decrease in area on pelleting was due to compression of some of the particles of the cobalt-promoter complex so that nitrogen molecules could not penetrate the spaces between them. After reduction granular catalyst 89K had the same area as reduced pelleted 89K. This is consistent with the previous hypothesis since reduction could cause enlargement of pores so that all of the surface would be accessible.

The data in Table II show the changes in surface area upon heating or evacuations at 400° and during the reduction. The area of the cobalt basic carbonate decreased considerably upon both heating and reduction. The area of the catalyst with kieselguhr but no promoters likewise decreased sizably both on heating and reduction, but not as greatly as the cobalt basic carbonate. The area of the promoted preparation without kieselguhr decreased sizably on heating but only slightly on reduction. The area of the catalysts with both promoters and carriers decreased less in both steps than other preparations, the greatest decrease occurring in the heating step. Thus the kieselguhr appeared to be somewhat effective in preventing sintering of the surface during the heating step and less effective during the reduction. The promoters were about as effective in preventing sintering in the heating step as the kieselguhr, but very effective in inhibiting sintering during reduction. The catalysts containing both promoters and carriers which combine both of the protective actions sinter least in both of the steps.

Changes in Densities and Pore Volumes on Reduction

In Table III the mercury densities determined at 1 atmosphere (under these conditions mercury

(20) Zettlemoyer and Walker, *Ind. Eng. Chem.*, **39**, 69 (1947).

should penetrate only pores larger than 5 microns in diameter²¹) show that preparations containing kieselguhr did not change in volume as measured by mercury on reduction, whereas the volume of mercury displaced by preparations without kieselguhr decreased considerably. This is shown in the last two columns of Table III. This agrees with the role of the kieselguhr postulated previously³—that the kieselguhr acts as a "brush-pile" which defines the volume of the catalyst particle.

It was found that the mercury wet the reduced cobalt basic carbonate (pure cobalt metal) to some extent, which, of course, invalidates the usual interpretation of mercury densities; however, this was the only sample upon which this phenomenon was observed. Presumably, the presence of promoters or kieselguhr prevents such wetting. Should this occur to a slight extent on all of the reduced catalysts, the general picture of the changes in volume on reduction would not be altered, since the changes in volume are easily observed visually.

The helium densities were less accurate than the mercury densities due to the small volume of helium displaced by the reduced catalysts. However, repeated determinations on the same sample usually agreed within 3%. With exception of the low helium density observed with the reduced cobalt-thoria-magnesium oxide preparation, for which we have no explanation except possibly incomplete reduction, the observed densities differed no more than 4% from those computed from the catalyst composition, assuming no solution or compound formation of the catalyst components.

The pore volumes of all the catalysts containing kieselguhr increased on reduction, but those of preparations without this carrier decreased. Average pore diameters were computed by the equation of Emmett and DeWitt¹⁹ for cylindrical open-end pores. Since the decreases in surface area were always greater than decreases in pore volume, the average pore diameters always increased on reduction.

Reduction was accompanied by a decrease in surface area and in some cases by a decrease in bulk volume. With unpromoted and unsupported cobalt, large changes occurred in both. When cobalt atoms are formed by reduction, they must be able to migrate until they find stable sites in the lattice of the already reduced metal. In fact, in the reduction of the cobalt oxide powder (Table I) for twenty-four hours at 250° hexagonal aggregates or possibly crystals of cobalt several microns in diameter were formed.¹⁰

Kieselguhr provides a framework which prevents the decrease in bulk volume on reduction and at the same time inhibits sintering of the surface. The cobalt-promoter complex probably shrinks about the kieselguhr particles, thus inhibiting the growth of large crystallites of cobalt.

The promoters, which at least in the case of

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

thoria and precipitated magnesia are thoroughly mixed with the cobalt basic carbonate, have a more intimate role than the kieselguhr. In the change from the basic carbonate to cobalt metal, the volume of the part containing the cobalt decreases several-fold. The cobalt atoms possibly retreat from the surface, leaving a matrix of the relatively unchanged promoter which inhibits migration of atoms and growth of large crystallites.

Chemisorption of Carbon Monoxide on Reduced Catalysts

In the research of Emmett and Brunauer^{11,22} the chemisorption of carbon monoxide at -195° was taken as an indication of the extent of iron present on the surface of the iron catalysts. Figure 2 shows typical isotherms of carbon monoxide and nitrogen at -195° on reduced cobalt catalysts and cobalt oxide powder plotted on a relative pressure basis. Since the physical properties of carbon

monoxide and nitrogen including molecular size are nearly identical, the nitrogen isotherm was taken equal to the physical carbon monoxide isotherm. The difference of the carbon monoxide (physical plus chemisorption) and nitrogen isotherms at equal relative pressures was taken as the volume of chemisorbed carbon monoxide. The constancy of these differences as shown in Fig. 2 demonstrates the correctness of this assumption. Emmett and Brunauer^{11,22} found that the ratio of the amount of chemisorbed carbon monoxide to the physically held monolayer, as determined by the B.E.T. method¹⁶ on pure iron, was 1.10 to 1.18, while on two nickel preparations Emmett and Skau²³ observed ratios of 0.92 and 1.78. Ratios slightly larger than one, such as observed on pure iron catalysts, may be explained by assuming the chemisorbed molecules to be more densely packed in the chemisorbed layer than in the physically held one. On reduced cobalt oxide powder and cobalt basic carbonate the ratios of chemisorbed carbon monoxide to the monolayer of physically held nitrogen were only 0.65. The reasons for these differences of these ratios for pure iron and cobalt are not known. However, Emmett²⁴ found that with highly sintered iron preparations this ratio was less than 1. The two pure cobalt preparations described in the present paper may be regarded as highly sintered.

An explanation which is probably greatly oversimplified may be given from the geometry of possible cobalt surfaces. Two of the possible crystal faces of α - and β -cobalt are shown in Fig. 3. If chemisorbed molecules are assumed to attach to the centers of the cobalt atoms, the size of the molecule will prevent adsorption on adjacent cobalt atoms. The resulting ratios of chemisorbed to physically held molecules will be 0.65 and 0.75 for the faces shown, which are near the ratios observed for cobalt metal in the reduced cobalt oxide powder and cobalt basic carbonate.

For the reduced cobalt-thoria-magnesia kieselguhr catalysts the ratios of chemisorbed carbon monoxide to the V_m value for the complex varied from 0.259 to 0.470, and for the cobalt-thoria-kieselguhr catalyst this ratio was 0.448. The ratios of chemisorbed carbon monoxide to the nitrogen-monolayer for cobalt-promoter and cobalt-kieselguhr preparations varied from 0.461 to 0.586. Cobalt-thoria preparations had higher ratios than those of cobalt-magnesia.

The ratio of chemisorbed to physically held molecules divided by the ratio for pure cobalt metal, 0.65, may not be an accurate indication of the extent of cobalt atoms in the catalyst surface, since, as shown in Fig. 3, all of the atoms adjacent to the cobalt atom adsorbing the carbon monoxide could be replaced by promoters without changing the ratio. In any case, the data of Table IV indicate that the surface of the catalyst with both pro-

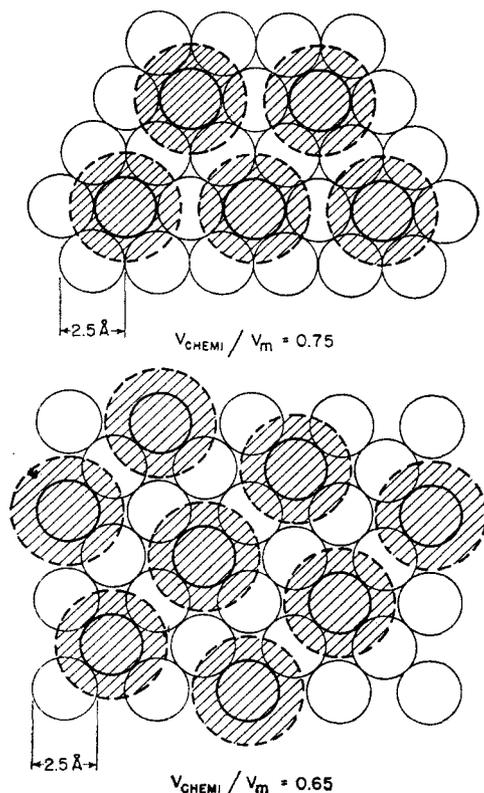


Fig. 3.—A representation of the manner that carbon monoxide may chemisorb on a cobalt surface. The upper drawing represents the closest packed faces of α - or β -cobalt, and the lower drawing the 100 faces of β -cobalt. Chemisorbed carbon monoxide molecules (the sectioned, dotted circles) are assumed to attach to the centers of cobalt atoms. The diameters of these circles give a cross sectional area of 16.2 sq. Å. per molecule in a close packed monolayer.

(22) Emmett and Brunauer, *THIS JOURNAL*, **57**, 1754 (1935); **59**, 310, 1553 (1937).

(23) Emmett and Skau, *ibid.*, **65**, 1029 (1943).

(24) Emmett, private communication.

moter and carrier must be covered to at least 30% by substances other than cobalt.

X-Ray Diffraction Patterns of Reduced Cobalt Catalysts

The diffraction patterns of this series of preparations in the reduced state show the effect of promoters (thoria and magnesia) and the support (kieselguhr) on crystallite size. The background due to scattering from the amorphous constituents of the catalysts, particularly thoria and kieselguhr, makes exact evaluation of line broadening difficult; nevertheless the trends are unmistakable. Reduced cobalt basic carbonate gave the sharpest diffraction pattern, but some line broadening corresponding to crystallites about 800 Å. diameter was observed. The most diffuse patterns were obtained from 108B, Co:MgO (100:12), Co:ThO₂:MgO (100:6:12), 89J and 89H. The line broadening of this group corresponded roughly to crystallites of 100–300 Å. The preparations Co:ThO₂ (100:6), Co:Filter-Cel (100:200), and Co:MgO (100:8) gave line broadening corresponding to crystallites 300–600 Å. diameter. These results are in general agreement with surface area measurements.

The diffraction patterns of many of these preparations lack expected reflections. This has been previously noted⁹ in connection with fully promoted and supported catalysts. The diffraction pattern of the reduced cobalt basic carbonate contained relatively strong 111, 200, 220, and 311 lines of face-centered cubic cobalt as well as faint 10 $\bar{1}$ 0 and 10 $\bar{1}$ 1 lines of hexagonal close-packed cobalt; such a pattern would normally be expected of a mixture of a relatively large amount of f.c.c. cobalt and a small amount of h.c.p. cobalt. With increasing amounts of promoter and support the 200-f.c.c. line and the 10 $\bar{1}$ 0- and 10 $\bar{1}$ 1-h.c.p. lines tend to disappear; in a fully promoted and supported catalyst, such as 89J and 108B, the 200-f.c.c. and 10 $\bar{1}$ 0- and 10 $\bar{1}$ 1-h.c.p. lines cannot even be identified with certainty. It is interesting to note that the persistent lines 111, 220, and 311 of f.c.c. correspond to 0002, 11 $\bar{2}$ 0, and 11 $\bar{2}$ 2 of h.c.p., respectively, in interplanar spacing. Among the partly promoted or supported preparations, those containing magnesia produced a weak but unmistakable 200-f.c.c. reflection, whereas neither the 10 $\bar{1}$ 0- or the 10 $\bar{1}$ 1-h.c.p. lines could be positively identified. The converse is true of those partly promoted or supported preparations containing no magnesia. A theoretical discussion of this phenomenon will be published shortly.

Discussion

Promoters may have two functions: first, that of maintaining or increasing the extent of the surface and, second, that of providing a surface of the proper physical or chemical nature. In some cases a single promoter may perform both of these functions and in other cases only one of them.

Russell and Taylor²⁵ showed that thoria as a promoter in nickel catalysts performed both of these functions. The surface area as estimated by the chemisorption of hydrogen and carbon dioxide was increased 20 to 40%, while the activity for hydrogenation of carbon dioxide to methane increased nine fold. Similarly, thoria in cobalt-thoria-kieselguhr catalysts may accomplish both of these functions. Alkali in precipitated- or fused-iron Fischer-Tropsch catalysts appears to alter the distribution of products but does not increase the surface area or activity appreciably. In doubly promoted (alumina-potassium oxide) synthetic ammonia catalysts, alumina is an effective structural promoter and potassium oxide is assumed to alter the chemical nature of the surface to inhibit formation of imide and amide groups on the surface.¹¹ The studies of Emmett and Brunauer¹¹ and others demonstrate these effects. The data in the present paper show chiefly the effect of promoters and carriers in maintaining surface area, but the X-ray diffraction and chemisorption data give some information as to the nature of the surface.

The chemisorption studies indicate that a sizable fraction of promoter was present on the catalyst surface. In addition to greater surface areas and surface stability of the promoted catalysts, the relatively isolated metal atoms or groups of atoms at the surface may have greater activity than that of crystallites of unpromoted metals.

The X-ray diffraction data were in qualitative agreement with surface-area measurements, but in addition revealed that the cobalt metal in promoted and supported catalysts had an anomalous crystal structure. The presence of the promoters and the support favored this anomalous structure. It should be noted that X-ray diffraction studies reveal the average structure of the crystallites of cobalt and not just the surface.

It has been suggested that kieselguhr as a carrier in cobalt and nickel catalysts produces the proper degree of dispersion of the active metal and gives the desired porosity.²⁶ The data in this paper demonstrate the manner in which these effects are accomplished. Kieselguhr provided a framework about which the metal oxide complex shrank when reduced to the metal. Kieselguhr also provided a system of large, accessible pores and appeared to prevent excessive decrease in the area of the metal. It should be noted that in our catalysts the cobalt-promoter complex was deposited chiefly in the pores of the kieselguhr that were larger than 5 microns.³

Upon reduction, the bulk volume of the catalyst containing kieselguhr remained unchanged, whereas the bulk volume of the unsupported catalyst decreased several fold. Kieselguhr as a carrier is important if the reaction is highly exothermic, as in the Fischer-Tropsch synthesis, or

(25) Russell and Taylor, *J. Phys. Chem.*, **29**, 1325 (1925).

(26) Hall, Craxford and Gall, "Interrogation of O. Roelen," British Intelligence Objectives Sub-Committee, 1945.

if the catalyst is reduced in the reactor. If the reaction is highly exothermic, the heat produced by a dense, unsupported catalyst may exceed the capacity of the reactor to remove the heat of reaction, and the catalyst may overheat. This is possibly the reason for the great improvement in life of cobalt and nickel Fischer-Tropsch catalysts when kieselguhr was used as a carrier.²⁷ Pichler²⁸ has stated that industrial development of the synthesis in Germany appeared possible only after the introduction of kieselguhr as a carrier for cobalt catalysts. If the catalyst is to be reduced in the converter, the large decrease in bulk volume on reduction of unsupported catalysts will cause a large amount of reactor space to be wasted.

Ries²⁹ and Visser and DeLange³⁰ have shown that unreduced catalysts of cobalt and nickel, respectively, precipitated in the presence of kieselguhr have considerably higher surface areas per gram of active metal than the unsupported catalyst. Visser and DeLange have shown the formation of hydrosilicate bonds between the nickel and kieselguhr. With our catalysts the presence of kieselguhr does not greatly increase the area of the unreduced catalyst, and there is very little evidence to indicate any reaction of cobalt with the kieselguhr. In fact, in the standard methods of preparing the cobalt catalysts these effects are minimized by keeping the time of contact of the reacting solutions with the kieselguhr as short as possible.

Craxford³¹ studied the rates of carbiding, hydrogenation of carbide and synthesis on cobalt-thoria-kieselguhr (100:18:100) catalysts and on similar preparations with thoria or kieselguhr or both omitted. The rate of hydrogenation of ethylene was taken as an indication of the surface area, and since these rates were of the same magnitude, it was assumed that the surface areas were about equal. Hence, Craxford concluded that

(27) Fischer and Koch, *Brennstoff Chem.*, **13**, 61 (1932); Fischer and Meyer, *ibid.*, **12**, 225 (1931).

(28) Pichler, "Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen," to be published by Hobart Publishing Co., Washington, D. C.

(29) Ries, *J. Chem. Phys.*, **14**, 465 (1946); also *Ind. Eng. Chem.*, **37**, 310 (1945); and *THIS JOURNAL*, **67**, 1242 (1945).

(30) Visser and DeLange, *De Ingenieur*, **58**, 24 (1946); DeLange, private communication.

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

thoria and kieselguhr do not act primarily by increasing the available cobalt area, but as specific promoters for formation and reduction of carbide.

The data presented in the present paper indicate that the differences in both total surface area (Table I) and area of cobalt (Table IV) are quite large. The volume of chemisorbed carbon monoxide per gram of complex varied roughly in the same manner as Craxford's activities for carbide formation and reduction and for the synthesis. The uncertainties of this comparison are large because: (a) in some cases the catalysts compared did not have the same composition, and (b) the methods of catalyst preparation may have been considerably different. However, we believe that this comparison shows the activities of Craxford's catalysts to be strongly a function of surface area.

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Summary

1. Reduced cobalt-thoria-magnesia-kieselguhr and cobalt-thoria-kieselguhr catalysts and similar preparations with one or more of the components omitted have been studied by nitrogen surface areas and carbon monoxide chemisorptions at -195° , mercury and helium densities, and X-ray diffraction.

2. The promoters were found to prevent excessive decreases in surface area on reduction.

3. Kieselguhr as a carrier was somewhat effective in preventing the decrease of surface area on reduction, but its most important function was to prevent the decrease in bulk volume of the catalyst on reduction.

4. The carbon monoxide chemisorption studies showed that an appreciable fraction of the surface was occupied by promoter.

5. The X-ray diffraction data were in qualitative agreement with the surface-area determinations, but in addition indicated that the cobalt in supported and promoted catalysts had an anomalous structure.

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