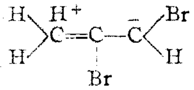
penes (2.2 and 0.84).[4] The fact that the *trans* forms of the propenes have as high moments as found must be due to interactions involving the methyl group, since the moments of the *trans* forms of the 1,2-dichloro- and 1,2-dibromoethylenes are both zero. Presumably charge-separated resonance isomers such as the following are involved



The *cis*-1,2-dibromopropene has a lower dipole moment than the corresponding chloropropene, while the result is reversed for the *trans* forms. The former result is in line with the fact that *cis*-1,2-dibromoethylene has a moment (1.35) lower than that of the corresponding dichloroethylene (1.89). The latter result could be explained if each isomer were contaminated with the other, and this is a possibility in view of the known isomerization. However, the distillations were carried out at low pressure and not far from room temperature. Since Van Risseghem showed that no isomerization of either form occurred after standing four days at room temperature in the absence of air, it seems reasonable to suppose that little isomerization took place in any part of the column during the collection of the sample. Moreover, if isomerization did occur, the lower boiling (*trans*) isomer should still have been pure. There was no indication that any appreciable isomerization occurred during the period of capacitance measurements.

An explanation of this anomaly may lie in the following. The difference (0.54) between the dipole moments of *cis*-dichloroethylene (1.89) and *cis*-dibromoethylene (1.35) represents the direct lowering of the dipole moment when bromine is substituted for chlorine in a *cis*-1,2-dihaloethylenic compound, for here no resonance into charge-separated isomers like that shown above is possible. The difference (0.32) in moment between the *trans*-dichloropropene (0.84) and the *trans*-dibromopropene (1.16) must be due to the increase in contribution of resonance isomers when bromine is substituted for chlorine in the 1,2-dihalopropene molecule, for the simple vector moments of the halogens in these compounds must cancel.

When one substitutes bromine for chlorine in the *cis*-1,2-dihalopropenes both the direct lowering of the moment as found in the *cis*-dihaloethylenes and the increase in moment due to resonance as exhibited in the *trans*-1,2-dihalopropenes should appear. The net decrease $(0.54 - 0.32 = 0.22)$ is in agreement with the experimentally observed quantity $(2.20 - 1.97 = 0.23)$. Exact agreement is probably fortuitous.

Summary

The isomeric 1,2-dibromopropenes have been obtained in a pure state, and their dipole moments have been measured. The results confirm the assignment of the *cis* structure to the higher boiling isomer. The moments have been compared with those of the corresponding dichloro compounds, and with the dichloro- and dibromoethylenes, and the differences discussed.

Knoxville, Tennessee Received May 29, 1950

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[4] W. H. King and H. A. Smith, This Journal, **72**, 3459 (1950); *cf.* H. A. Smith and W. H. King, *ibid.*, **70**, 3528 (1948).

[Contribution of the Research & Development Branch, Office of Synthetic Liquid Fuels, Bureau of Mines]

Studies of the Fischer–Tropsch Synthesis. VIII.[1] Surface Area and Pore Volume Studies of Iron Catalysts

By W. Keith Hall, William H. Tarn and Robert B. Anderson

This paper reports the changes in surface area and pore volume during the reduction of two widely different iron catalysts, a precipitated Fe_2O_3–CuO–K_2CO_3 catalyst and a fused Fe_3O_4–MgO–K_2O catalyst. The studies provide information as to the nature of iron catalysts at the start of the Fischer–Tropsch synthesis, as well as data pertinent to the mechanism of reduction. Previous papers have presented data describing the surface area and pore volumes of cobalt Fischer–Tropsch catalysts.[2,3,4]

Phase relations of the iron–oxygen system have been presented by Kelly,[5] and the thermodynamics of the reduction of iron oxide were discussed by Emmett and Shultz.[6] Udy and Lorig,[7] Meyer[8] and Tennenbaum and Joseph[9] have reported data pertinent to the mechanism of the reduction, and Brunauer and Emmett[10] have reported changes in surface area that occur

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[1] Part VII of this series Anderson, Shultz, Seligman, Hall and Storch, This Journal, **72**, 3502 (1950).

[2] Anderson, Hall, Hewlett and Seligman, *ibid.*, **69**, 3114 (1947).

[3] Anderson, Hall and Hofer, *ibid.*, **70**, 2465 (1948).

[4] Anderson, Hall, Krieg and Seligman, *ibid.*, **71**, 183 (1949).

[5] Kelly, Bureau of Mines, Bulletin 296, Iron Oxide Reduction Equilibria.

[6] Emmett and Shultz, This Journal, **52**, 4268 (1930); **55**, 1376 (1933).

[7] Udy and Lorig, *Metals Technology*, T. P. 1509 (1942).

[8] Meyer, K. W. I. Band 10 (1928), "Von die Reduktionsgeschwindegheit von Eisenerzen in Strömenden Gasen."

[9] Tennenbaum and Joseph, *AIMME Transactions*, **135**, (1939).

[10] Brunauer and Emmett, This Journal, **59**, 310, 1553, 2682 (1937); **62**, 1732 (1940).

in the reduction of iron synthetic–ammonia-type catalysts.

Experimental

The fused catalysts studied, D3001 and D3006, were prepared by fusing a mixture of iron oxide and promoters in a conduction-type furnace.[11] Preparation of the precipitated catalysts, P-3003.24 and P-3003.042, was adapted from methods described by Pichler.[12] A hot solution of sodium carbonate was added to a hot "pre-neutralized" solution of ferric and cupric nitrates. The nitrate solution was stirred vigorously, and the precipitation was accomplished as rapidly as possible. The precipitate was washed free of soluble salts with distilled water[13] and then alkalized with the appropriate amount of potassium carbonate before drying and crushing to the desired size. The chemical analysis of the finished catalysts studied are given in Table I.

TABLE I

PERCENTAGE COMPOSITION OF CATALYSTS

Component	Catalyst number			
	D-3001	D-3006	P-3003.24	P-3003.042
Total Fe	66.8	66.9	57.6	54.1
SiO_2	0.6	0.6	...	...
Cr_2O_3	0.8	0.8	...	...
MgO	4.6	4.6	...	...
Cu	..	..	5.8	5.1
K_2O	0.6	0.5	0.3	0.3
Mesh size	6–8	4–6	6–14	6–10

In the studies of catalysts D-3001, P-3003.24 and P-3003.042 reduction and sintering were carried out in Pyrex adsorption and density tubes equipped with special four-way stopcocks.[3,14] To facilitate charging and removing the sample without changing the volume of the vessel, the charging tube shown previously was extended to the level of the stopcock and closed with a ground-glass joint. After filling the tube, a close-fitting glass rod was inserted into the charging tube to minimize the dead space. These vessels were heated in a horizontal position in a small resistance furnace controlled automatically to ±3°.[3] The loss in weight of sample was followed by weighing the entire tube on an analytical balance.

Because some of the temperatures employed in reducing catalysts of the D-3006 series were too high for Pyrex glass, the entire series was reduced in a steel-lined aluminum block furnace.[1] At the end of these reductions, the sample was cooled to room temperature in H_2; CO_2 was then passed over the sample during its removal to an appropriate transfer flask, from which the catalyst could be conveyed under CO_2 to adsorption and density tubes or sampled for analysis. To remove chemisorbed CO_2 or traces of oxygen acquired in the transfer, the samples received an additional reduction in H_2 at 450° to constant weight in the adsorption tubes. All samples were evacuated to pressures less than 10^{-4} mm. for about 30 minutes at their final reduction or sintering temperatures before the adsorption or density experiments were made.

Dry electrolytic H_2 freed from traces of O_2 and water vapor by passing over hot copper (in some cases a "Deoxo" tube) and anhydrous $Mg(ClO_4)_2$ was used in the reductions. In one experiment, H_2 saturated with water vapor at room temperature was used to reduce a sample only from Fe_2O_3 to Fe_3O_4.

Nitrogen isotherms at −195° were determined by the conventional volumetric method.[15] Surface areas were estimated by the use of the simple BET equation[16] with the cross-sectional area of the adsorbed nitrogen molecule assumed to be 16.2 A^2. Carbon monoxide isotherms were determined at −195°, and the volume of chemisorbed carbon monoxide was assumed to be the difference between the CO and N_2 (which does not chemisorb at this temperature on these catalysts) isotherms plotted on a relative-pressure basis. Mass spectrometric analysis showed all of the gases to be of greater purity than 99.7%. Densities determined by displacement of mercury and densities determined by displacement of helium were obtained at pressures of 1,150 and 760 mm., respectively, by methods described previously.[17] Both density measurements were made on the same sample of catalyst. After mercury-density determination, the reduced samples were examined carefully, but no indication of wetting of iron by the mercury was observed.[18]

Results

Sintering and Reduction of Precipitated Catalyst P-3003.24.—Many precipitated-iron Fischer–Tropsch catalysts have gel-like structures.[19,20] However, reduction of these catalysts in H_2 or induction[21] in synthesis gas decreased their areas by a factor of 10 to 30. For example, the area of ferric oxide catalyst 10K[20] decreased from 169 to 9 sq. m./g. on reduction in H_2 at 360°[20] and the area of catalyst P-3003.042 decreased from 303 to 23 sq. m./g. in a pretreatment with $1H_2{:}1CO$ gas at 230°. Several experiments were made to determine whether these changes were produced by thermal sintering or whether they occurred in the reduction process.

Data for nitrogen adsorption measurements at −195° are presented in Fig. 1 and Table II. The isotherms in Fig. 1 show that the average pore diameter increased rapidly[22] and the surface area decreased as the catalyst was sintered in N_2 at increasing temperatures. Isotherms of samples sintered at temperatures up to 450° were type IV of Brunauer's classification,[23] and those of samples sintered at higher temperatures or reduced in H_2 were type II. Reduction to magnetite or iron (samples 6 and 5) produced about

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(11) For a typical method of preparation of synthetic ammonia catalyst, see Bridges, Pole, Beinlich and Thompson, *Chem. Eng. Progress*, **43**, 291 (1947).

(12) H. H. Pichler, Bureau of Mines Special Report.

(13) Residual Na_2O content of about 0.07% was found in each case.

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

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

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

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

(18) Wetting by Hg was observed only on pure Fe formed in the reduction of unpromoted catalysts.

(19) Anderson and Hall, THIS JOURNAL, **70**, 1727 (1948).

(20) Storch, *et al.*, Synthetic Liquid Fuels from Hydrogenation of Carbon Monoxide, Part 1, Bur. Mines Tech. Paper 709, 171 (1948).

(21) Induction is a pretreatment step used to activate precipitated catalysts for the Fischer–Tropsch synthesis. Besides reduction of the ferric iron gel to Fe_3O_4, part of the iron is converted to iron carbide, Fe_2C.

(22) This is inferred from the Kelvin equation

$$\ln \frac{p}{p_0} = \frac{-2\sigma V \cos \theta}{r RT}$$

where σ is the surface tension, θ is the contact angle, V is the molar volume, R is the gas constant, T is the absolute temperature, r is the pore radius and p/p_0 is the relative pressure. Everything else being constant, r increases as p/p_0 increases (see reference 26).

(23) Brunauer, THIS JOURNAL, **62**, 1723 (1940).

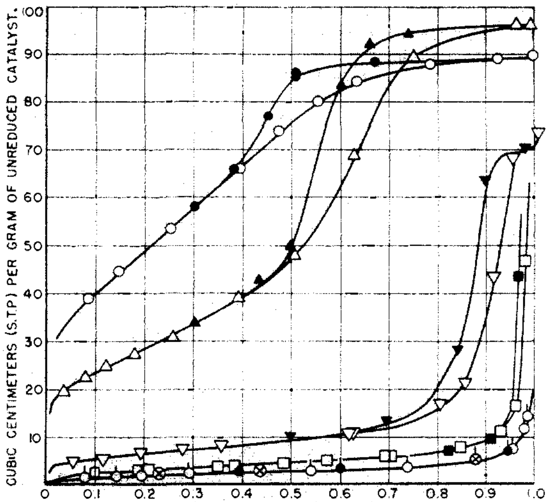

Fig. 1.—Nitrogen adsorption isotherms of catalyst P-3003.24 at −195° after heat treatment and reduction: The catalyst after evacuation at 100° is represented by ○, after heating in N_2 at 300° by △, after heating at 450° by ▽, after heating at 550° by ⊗, after converting to Fe_3O_4 by reduction at 250° with H_2 saturated with H_2O vapor by □, and the sample after heating at 300° (△) followed by reduction in H_2 at 300° by Ó. Adsorption points are open and desorption points are solid.

the same large change in the isotherm as sintering at 550°. Experiments were made to determine if the glow phenomena[24] occurred when the catalyst was heated in air to 550°, but results were inconclusive. X-Ray diffraction patterns of the treated materials showed those sintered in N_2 to be Fe_2O_3, those reduced in H_2 saturated with H_2O vapor to be Fe_3O_4 + Cu, and those reduced with pure dry H_2 to be mainly α-Fe and Cu with some residual Fe_3O_4.

Table II

Isotherm Data of Heat-treated and Reduced Precipitated Catalyst P-3003.24

Sample	Treatment Gas	Temp., °C.	Time, hr.	Weight loss, %	Type of isotherm[a]	Area, sq. m./g. of unreduced catalyst	V_s[b] cc. of liquid N_2 g. unreduced catalyst
1	Evac.	100	1	1.7	IV	184.0	0.140
2	N_2	300	16	5.0	IV	97.4	.150
3	N_2	450	16	5.9	IV	23.4	.110
4	N_2	550	16	6.4	II	8.4	...
5[c]	H_2	300	17	33.0[d]	II	6.3	...
6	H_2-H_2O[e]	250	19	9.2	II	11.3	...

[a] See reference 23 of text. [b] Nitrogen adsorbed at p_0. [c] Sample after treatment 2. [d] Sum of 2 + 5. [e] H_2 gas was saturated with H_2O at 26°.

The samples used to obtain the density measurements shown in Table III were treated in the same way as those in Table II. The helium densities increased toward the calculated density of a mixture of hematite and copper oxide (5.21) as the temperature of sintering was increased. The helium density of the sample reduced with hydrogen containing water vapor was 5.25, compared with 5.35 for a mixture of magnetite and copper. Reduced sample 11 had a density of 7.60, compared with 7.98 for a mixture of iron and copper. The volume of mercury displaced per gram of unreduced catalyst (Column 8, Table III) decreased with increasing sintering temperature. Reduction to magnetite caused about the same decrease in this volume as heating in nitrogen at the same temperature, but reduction to iron in dry H_2 caused a greater decrease in volume than heat treatment in nitrogen at 550°. The decrease in the volume of mercury displaced may result from a decrease in the bulk volume of the particles or from the formation of pores large enough to permit penetration by mercury.[25] The former is probably the most important effect, as the bulk volume of the catalyst was observed to decrease in treatments with nitrogen or hydrogen. The pore volumes, obtained as the difference between the volume of helium and the volume of mercury displaced, were in general agreement with those computed from the flat upper portions of the type IV isotherms, with the assumption that the adsorbed nitrogen has the same density as normal liquid. The pore volume increased when the catalyst was heated in nitrogen to 300° but decreased as the catalyst was heated to higher temperatures. The first increase was probably due to the removal of water accompanied by only slight sintering of the pore structure, but at 450° considerable sintering of the pore structure occurred. At 550°, and to an even greater extent in the reductions, the pore structure is drastically altered. After reduction in dry hydrogen, the pore volume was increased to 0.155 cc./g., a value greater than that of the original catalyst. The average pore diameter in Table III increased by a factor of 35, in agreement with the shapes of the isotherms in Fig. 1.

Studies of Fused Catalysts D-3001 and D-3006.—The variation of the extent of reduction of catalyst D-3001 at 450° with time is shown in Fig. 2. The circles represent the changes in a sample reduced progressively for adsorption studies, and the squares represent separate reductions of individual samples for pore volume measurements. The good reproducibility justifies combining the two sets of data in calculating pore diameters as a function of the extent of reduction.

The upper curve of Fig. 3 (open circles) shows the surface area per gram of unreduced catalyst as a function of the extent of reduction at 450°. The surface area increased linearly with the extent of reduction to about 90%. Above this value, the slope decreases and becomes negative near

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(24) Weiser, "Inorganic Colloid Chemistry," Vol. II, John Wiley and Sons, New York, N. Y., 1935, p. 22.

(25) Larger than about 5 microns in diameter, *cf.* Ritter and Drake, *Ind. Eng. Chem., Anal. Ed.*, **17**, 782 (1945).

TABLE III

MERCURY AND HELIUM DENSITIES, PORE VOLUMES AND PORE DIAMETERS OF CATALYST P-3003.24

Sample	Treatment				d_{Hg},[a] cc./g.	d_{He}, cc./g.	Volumes displaced[b]; cc./g. of unreduced catalyst		Pore volume,[c] cc./g. of unreduced catalyst	Pore diameter[d] $\bar{d}$, Å.
	Gas	Temp., °C.	Time, hr.	Weight loss, %			V_{Hg}	V_{He}		
7	Evac.	100	1	1.6	2.83	4.43	0.347	0.222	0.125	27
8	N_2	300	16	5.5	2.79	4.84	.338	.196	.151	59
9	N_2	450	16	6.1	3.14	5.04	.299	.186	.113	193
10	N_2	550	16	6.5	3.20	5.11	.293	.183	.109	519
11	H_2	300	17	32.6	2.73	7.60	.247	.089	.155	968
12	H_2–H_2O	250	18	12.7	2.75	5.25	.317	.166	.151	536

[a] Determined at an absolute pressure of 1100 mm. [b] $V_x = (1 - f)/d_x$, where d_x is the helium or mercury density, and f is the fractional weight loss on treatment. [c] Difference between the volume of Hg and He displaced. [d] $\bar{d}$ = 4(pore volume)/surface area, surface areas obtained from Table II, (*cf.* reference 26).

100% reduction. Point *a* corresponds to 99.4% reduction in 63 hours, and points *b* and *c* to complete reduction in 85 and 116 hours, respectively. The curve just below this (open triangles) is a similar plot of the chemisorbed carbon monoxide per gram of unreduced catalyst. This curve also increases linearly up to about 85% reduction, beyond which point the curve bends sharply upward. This behavior is a characteristic that must be explained in any postulated reduction mechanism. The solid circles and triangles found in the lower two curves present similar data for samples of this catalyst reduced at 550° and show the general effects of changing the reduction temperature.

The experimental density data are plotted in Fig. 4. The density and adsorption data in Table IV have been taken from the curves in Figs. 3 and 4. In Fig. 5, however, which shows the pore volume as a function of the extent of reduction, actual experimental points have been plotted. Column 4 of Table IV lists volumes of mercury displaced by reduced catalysts per gram of unreduced material. These volumes are essentially the same for all extents of reduction, which is interpreted as indicating that the external volume of the catalyst particle does not change during reduction and that mercury does not penetrate any of the pores. This explanation was substantiated by the observation that the linear dimensions, by direct measurement, of polished pieces of catalyst before and after reduction remained a constant.

The average pore diameters in Table IV were calculated on the basis of cylindrical open-end pores by the equation of Emmett and DeWitt.[26] From 20 to 95% reduction, $\bar{d}$ varied from 330 to 348 Å. but increased to 371 Å. as the reduction approached 100%. The value of $\bar{d}$ for 10% reduc-

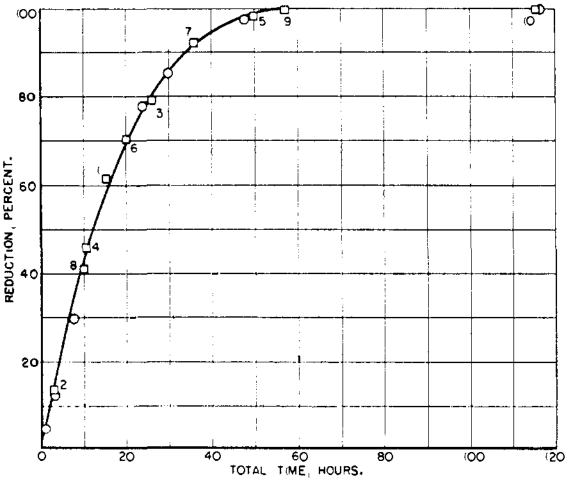

Fig. 2.—Extent of reduction of catalyst D-3001 at 450° and 1000 space velocity as a function of time: circles represent data taken progressively on a single sample for surface area measurements and squares represent independent determinations on separate samples for pore volume measurements. The numbers refer to the order in which the samples were reduced.

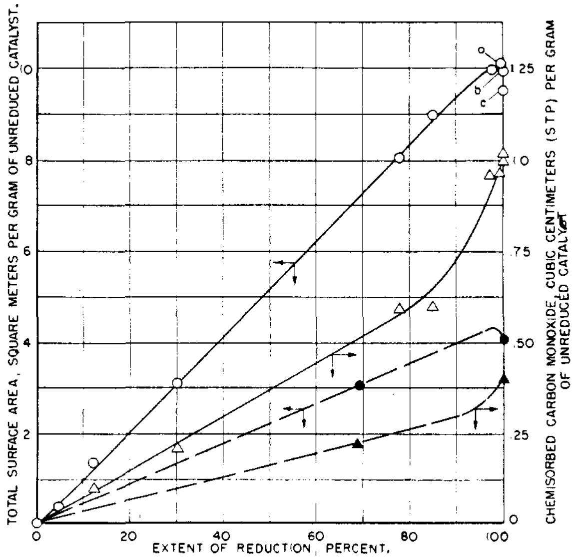

Fig. 3.—Variation of surface area and of carbon monoxide chemisorption with extent of reduction. The surface areas of samples reduced at 450° are represented by O and their carbon monoxide chemisorptions by △. The solid points represent samples reduced at 550°.

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

TABLE IV

DENSITY AND ADSORPTION DATA OF CATALYST D-3001 AS A FUNCTION OF THE EXTENT OF REDUCTION[a]

Redn., %	d_{He}, cc./g.	d_{Hg},[b] cc./g.	Vol.[c] of Hg displaced, cc./g. unreduced catalyst	Pore[d] vol., cc./g. unreduced catalyst	$\bar{d}$[e], Å.	Surface area, m.²/g. unreduced catalyst	V_m[f], (NTP), cc./g.	V_{CO}[g], (NTP), cc./g.	V_{CO}/V_m
0.0	4.96	4.91	0.203	0.002	. . .	0.0	0.0	0.0	. .
10.0	5.07	4.80	.203	.010	400	1.0	.23	.09	0.39
20.0	5.18	4.68	.203	.018	343	2.1	.48	.16	.33
30.0	5.32	4.56	.203	.027	348	3.1	.71	.22	.31
40.0	5.45	4.45	.202	.035	333	4.2	.96	.29	.30
50.0	5.60	4.33	.204	.043	331	5.2	1.29	.36	.28
60.0	5.77	4.22	.201	.052	330	6.3	1.44	.43	.30
70.0	5.98	4.10	.200	.061	334	7.3	1.67	.50	.30
80.0	6.22	3.98	.200	.071	338	8.4	1.92	.57	.30
90.0	6.50	3.87	.199	.082	349	9.4	2.15	.67	.31
95.0	6.65	3.81	.199	.086	348	9.9	2.26	.83	.37
100.0	6.82	3.75	.198	.089	352	10.1	2.31	1.00	.43
100.0[h]	6.82	3.78	.197	.088	371	9.5	2.20	1.00	.45
100.0[i]	6.95	3.71	.201	.094	917	4.1	0.94	0.38	.40
68.9[i]	. . .	. . .	. . .	. . .	832[k]	3.1	0.71	0.22	.31
KCl[j]	1.983	1.978		.000					
	1.984	. . .							

[a] All reductions were made with a flow of 1000 volumes of pure H_2 gas per volume of catalyst space per hour and at 450° except where otherwise noted. The catalyst was in all cases 6 to 8 mesh. [b] Determined at an absolute pressure of 1100 mm. [c] $V_x = (1 - f)/d_x$, where d_x is the helium or mercury density and f is the fractional weight loss on treatment. [d] Difference between the volume of Hg and He displaced. [e] $\bar{d}$ = 4(pore volume)/surface area (*cf.* reference 26). [f] Volume of nitrogen corresponding to a monolayer per gram of unreduced catalyst. [g] Volume of carbon monoxide chemisorbed at −195° per gram of unreduced catalyst. [h] This row of data was obtained on a sample reduced for 116 hours at 450°. [i] These data were obtained on samples reduced at 550°. [j] KCl was used to check our calibrations; the observed values are shown in the upper row and the literature value is below. [k] Calculated, taking the pore volume from equation 4.

tion may be regarded as somewhat uncertain, because both the surface area and the pore volume are small. It has been shown[19] that this pore diameter must be considered as an upper limit of the real diameter.

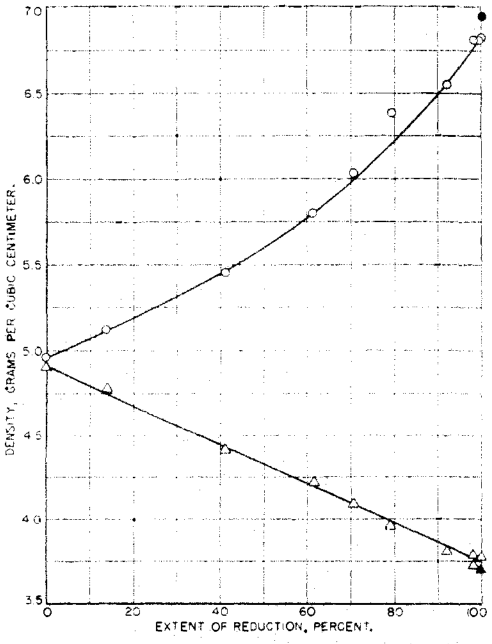

Fig. 4.—Variation of mercury and helium densities with extent of reduction: Absolute densities of catalysts reduced at 450° measured by displacement of He, are represented by O: their densities measured by displacement of Hg are represented by △. Solid points represent a 550° reduction.

The variation of surface area and pore volume with reduction temperature for completely re-

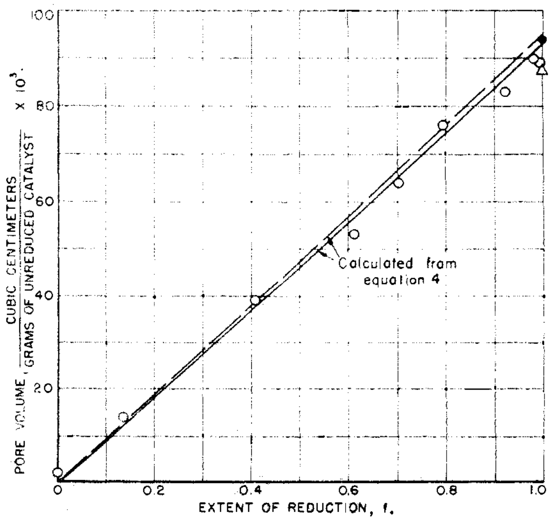

Fig. 5.—Variation of pore volume per gram of unreduced catalyst with extent of reduction of catalyst D-3001, where O represents reduction at 450°, ● represents reduction at 550° and △ represents a 115-hour reduction and sintering at 450°.

duced samples of catalysts D-3001 and D-3006 is shown in Table V. The pore volumes and the volumes of mercury displaced by the reduced samples per gram of unreduced catalyst remained essentially constant, whereas the surface area decreased from 10.1 to 1.6 sq. m./g., and the average pore diameter increased from 366 to 2,420 Å. as the temperature of reduction was increased from 450 to 650°. The ratio $V_{\mathrm{CO}}/V_{\mathrm{m}}$ was essentially constant at about 0.3 for the D-3006 series. This value was lower than those of the completely reduced D-3001 samples.

TABLE V

DENSITY AND ADSORPTION DATA OF SYNTHETIC AMMONIA-TYPE CATALYSTS AS A FUNCTION OF REDUCTION TEMPERATURE[a]

Catalyst	Redn. temp.,[b] °C.	V_{m}, cc. (STP)/g.	V_{CO}, cc. (STP)/g.	$V_{\mathrm{CO}}/V_{\mathrm{m}}$	Surface area, sq. m./g.	Vol. of Hg displaced, cc./g.	Pore[c] volume, cc./g.	$\bar{d}$[d], Å.
D-3001	450	2.31	1.00	0.43	10.1	0.198	0.089	371
D-3001	550	0.94	0.38	.40	4.1	.201	.094	917
D-3006	450	2.15	.72	.34	9.4	.194	.086	366
D-3006	500	1.21	.42	.35	5.3	.198	.091	687
D-3006	550	1.02	.32	.31	4.5	.195	.090	800
D-3006	600	0.46	.10	.22	2.0	.193	.092	1840
D-3006	650	.38	.12	.32	1.6	.199	.097	2420
D-3006[e]	...	..	..	..	..	.201	...	..

[a] All data given in terms of grams of unreduced catalyst. [b] The D-3006 samples were 4- to 6-mesh U. S. Standard screen fractions reduced in pure dry H_2 flowing at a rate of 2,000 volumes of gas per volume of catalyst space per hour. [c] Difference between the volume of Hg and He displaced. [d] $\bar{d} = 4$(pore volume)/surface area, (*cf.* ref. 26). [e] This was an unreduced sample.

Discussion

The surface-area and pore-volume data obtained for two types of iron Fischer–Tropsch catalysts show that the surface areas and pore volumes of fused catalysts are created in the reduction, whereas precipitated catalysts initially have large surface areas which decrease as reduction proceeds. It is interesting to note that, although these types of catalysts are vastly different in the raw state, after reduction their surface areas and pore volumes are very similar. Precipitated catalyst P-3003.24 is principally a ferric oxide gel. When heated in nitrogen at 300° the sample lost water and the pore volume increased. Heating in nitrogen at higher temperatures caused only a slight additional decrease in weight but caused the pore volume to decrease from the maximum value observed at 300°. The surface area decreased progressively as the temperature of sintering was increased. As the changes in pore volume were relatively small with respect to the decrease in surface area, the average pore diameter increased monotonically with increasing sintering temperature. When the sample was reduced only to magnetite at 250° in hydrogen saturated with water vapor at room temperature, the pore volume increased, whereas the surface area decreased about as much as that observed in sintering at 550°. The ferric oxide gel is much more stable to thermal sintering than to reduction. Presumably reduction, even to magnetite, causes a major re-orientation of the structural geometry. Reduction to iron at 300° caused a greater decrease in area, and again the pore volume increased. The volume of the particles, as indicated by the volume of mercury displaced, decreased in all sintering or reduction steps, the greatest change being observed in the sample reduced to iron. The sintering of ferric oxide gel catalysts during reduction is of significance to the Fischer–Tropsch synthesis, because these catalysts are reduced, at least to magnetite, either in the pretreatment or in the subsequent synthesis.

A simple explanation of the changes that occur in the reduction of fused iron catalysts involves the following premises: (1) the external volume of the particles does not change in the reduction; the pore structure of the catalyst is produced by the removal of oxygen. (2) Once initiated in a portion of the catalyst, the reduction proceeds very rapidly in that portion nearly, but not quite, to completion. The reduction proceeds directly from Fe_3O_4 to Fe, which is in accord with thermodynamic data.[5] (3) At 450° the reduced portion is quickly transformed to a relatively stable structure with an average pore diameter of 330 Å. (4) On a macroscopic scale, the reduction begins at the surface and moves uniformly inward. The rate data in Fig. 2 are satisfactorily approximated by an equation derived for spherical particles, assuming that the reduction proceeds uniformly inward from the external surface and that the rate is proportional to the area of the sphere of unreduced catalyst. This mechanism is substantiated by the photographs of polished sections of partly reduced particles of magnetite of Udy and Lorig.[7] These demonstrated that the Fe-Fe_3O_4 interface moved uniformly inward with the time of reduction.

On the basis of premises 1 and 2, the pore volume should increase linearly with extent of reduction (Fig. 5). Up to 90% reduction, the surface area also increased linearly (Fig. 3), indicating the formation of pores of constant diameter. This predicts that a plot of surface area against pore volume should be linear, as shown in Fig. 6. The slope of the linear portion of the curve corresponds to an average diameter of 333 Å. At reductions greater than 80% the average pore diameter increases, since the surface area increases less rapidly than the pore volume.

From premises 1 and 2 it is apparent that calculation of the pore volume at any extent of reduction is possible if the initial and final densities are known. Consider 1 g. of unreduced material composed of Fe_3O_4 and inert (unreducible) material. On reduction, part of the oxide changes to metallic iron and

$$\text{Pore volume} = V_0 - V_x \qquad (1)$$

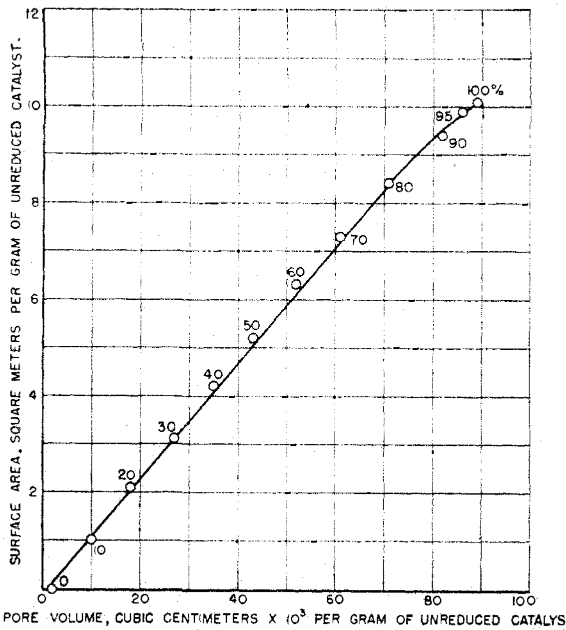

Fig. 6.—Variation of surface area with pore volume: the numbers indicate the extent of reduction.

where V_0 is the initial volume per gram and V_x the actual (helium) volume per gram of unreduced material after reduction to some fraction, f, of complete reduction. If the volume contributions of the constituents are additive

$$V_x = \sum_{\substack{\text{all}\\\text{phases}}} V_i = \sum_{\substack{\text{all}\\\text{phases}}} m_i/d_i \qquad (2)$$

where V_i, m_i and d_i are the volume and mass per gram of unreduced catalyst, and the absolute density, respectively, of component i. The volumes of iron and magnetite may be evaluated in terms of the initial and final volumes of the catalyst V_0 and V_F, respectively, and if the volume of the unreducible portion is V_b, then

$$V_x = (V_F - V_b)f + (1 - f)(V_0 - V_b) + V_b = V_0 + (V_F - V_0)f \qquad (3)$$

and from equations 1 and 3

$$\text{Pore volume} = (V_0 - V_F)f \qquad (4)$$

The solid line in Fig. 5 is a plot of equation 4, with V_0 and V_F evaluated from helium densities of the original and the completely reduced catalyst. The agreement with the experimental data is satisfactory. It is also possible, however, to compute V_0 and V_F from the densities of the phases present in the catalyst and from their weight fractions by equation 2. The dashed line in Fig. 5 was determined in this manner.

The increase in the ratio of chemisorbed carbon monoxide to the nitrogen monolayer as the reduction nears completion may result from removal of the last portions of residual iron oxide from the "reduced" part of the catalyst. Between 99.5 and 100% reduction, where the slope of the chemisorbed carbon monoxide curve was the greatest, about 1 additional carbon monoxide molecule was chemisorbed for every 100 iron atoms produced. The surface area of the catalyst decreased in this range, and the data suggest that the residual iron oxide may act as a structural promoter. This may also be attributed, however, to sintering during the long reduction period. The significant fact is, nevertheless, that the decrease in surface area occurs simultaneously with the increase in the V_{CO}/V_m ratio.

The effect of increasing the reduction temperature from 450 to 550° on catalyst D-3001 is shown in Fig. 3. At 550°, the reduced portion is transformed to a stable structure with an average pore diameter of 830 Å., about 2.5 times the diameter of the 450° reduction. At about 70% reduction, the ratios of V_{CO}/V_m are nearly identical for both temperatures of reduction.

The external volume of the particles of D-3006 (Table V) remained unchanged in reductions at temperatures up to 650°. However, the surface area decrease sizably as the reduction temperature increased, and, as the pore volume remained essentially constant, the average pore diameter varied in an inverse manner. Reduced pure, fused magnetite has a low surface area, about 1.0 sq. m./g. when reduced at 375°. The presence of structural promoters, MgO, SiO_2 and possibly Cr_2O_3, in catalysts D-3001 and D-3006 stabilized the surface formed in the reduction so that moderately high surface areas were attained at reduction temperatures as high as 650°. The presence of these promoters, however, does not prevent a decrease in area with increasing temperature of reduction. For catalysts of this type, variation of the temperature of reduction affords a method of "tailor-making" catalysts of any desired pore diameter over a relatively wide range. As the pore volume can be computed from equation 4, calculation of the average pore diameter requires only the determination of the surface area. In a subsequent paper, the relationship between average pore diameter and activity in the Fischer–Tropsch synthesis will be discussed for these and other catalysts.

Acknowledgments.—The authors acknowledge the assistance of Karl Stein who prepared some of the catalysts used here, and Wesley Dieter and Dr. W. Oppenheimer who analyzed the catalysts. Thanks are extended also to Dr. R. A. Friedel for the mass spectrometric analysis for purity of the gases used and to W. C. Peebles for making and identifying the X-ray diffraction patterns.

Summary

1. The surface areas of raw precipitated iron gel catalysts are high, and their pore diameters are small; conversely, unreduced iron–synthetic-ammonia-type catalysts have essentially no

surface area and no pore volume. After reduction at 300 and 450 to 550°, respectively, both types have moderate surface areas of about 8 sq. m./g. and reasonably large pore diameters of 350 to 900 Å.

2. Thermal sintering of precipitated iron gels causes drastic changes in structure, but removal of oxygen by reduction produces an even greater effect.

3. The surface area and pore volume of an iron–synthetic-ammonia-type catalyst increased in a linear manner with extent of reduction, whereas the average pore diameter remained constant.

4. It is shown that only surface area measurements and complete chemical analysis of the raw catalyst are necessary to establish the pore structure of an iron–synthetic-ammonia-type catalyst as a function of the extent of reduction.

5. Increasing the reduction temperature of an iron–synthetic-ammonia-type catalyst from 450 to 650° produced an eightfold increase in the pore diameter.

BRUCETON, PA.

RECEIVED APRIL 29, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Heat Capacity of Organic Vapors. VII. A Flow Calorimeter Requiring Only 25 Ml. of Liquid Sample

BY ALLAN E. REYNOLDS[1] AND THOMAS DE VRIES

In the program for measuring the heat capacity of organic vapors, a calorimeter was desired when the quantity of liquid is limited to 25 ml. Since the flow method of Callendar and Barnes is capable of giving highly reliable heat capacities[2,3,4] an apparatus was developed based on this principle. The accuracy of the colorimeter was checked by measuring the heat capacity of benzene for comparison with the data of Scott, *et al.*[3] The heat capacities for the three butyl alcohols were determined at 1 atm. pressure at 135 and 160°.

Experimental

Apparatus.—The main section of the calorimeter (see Fig. 1) was about 10 cm. long and 1 cm. in diameter, drawn to a wall thickness of 0.3 mm. to permit a minimum of time lost in reaching thermal equilibrium. The heater consisted of chromel wire wound into a helix on a $^3/_{16}''$ mandrel and supported on a strip of mica. The copper lead-out wires were also wound into helices to present a greater opportunity for the incoming vapor to take up the heat energy which otherwise would be conducted out through the leads. The copper wires were brought out through short sections of 1 mm. o. d. platinum tubing sealed into the walls of the calorimeter and closed with soft solder. This method for bringing wire through the glass and maintaining vacuum tight seals was found entirely satisfactory.

The outside of the calorimeter was given a bright platinum mirror finish. A saturated solution of dry platinum chloride in 95% ethanol was dissolved in five times its volume of oil of lavender. This solution was brushed on the clean glass parts and heated over a low flame of a Bunsen burner. The operation could be repeated if a thicker mirror was desired.

A triple junction thermel of copper and constantan wire was used to measure ΔT. An extra thermocouple was used to measure the temperature of the incoming vapor.

The calorimeter was mounted inside a copper jacket which could be evacuated. A heating element was wound on the jacket as well as a temperature sensitive element to control the temperature. The grid-controlled Thyratron thermoregulator designed by Sturtevant[5] was used. The thermometer element was made of vanadium–steel wire. Jacket temperatures could be held constant within a few hundredths of a degree over long periods of time.

A flash boiler was devised to evaporate the sample injected into it at a constant rate from a 30-ml. hypodermic syringe. The boiler assembly was made by sintering ground glass in a 7 mm. Pyrex glass tube. The annular space between this tube and an outer 28 mm. tube was filled with mercury and kept about 20° above the boiling point of the liquids studied. Rapid and smooth evaporation of the sample occurred. The speed of sample injection could be varied from 0.6 to 9.1 ml. per min. by a screw drive geared to a variable speed motor. A revolution counter was geared to the screw drive to measure the volume of sample delivered. Volumes could be measured with a precision of 0.1%. The rate of flow was timed with a hand operated stop watch, which was checked against the time signals from the National Bureau of Standards.

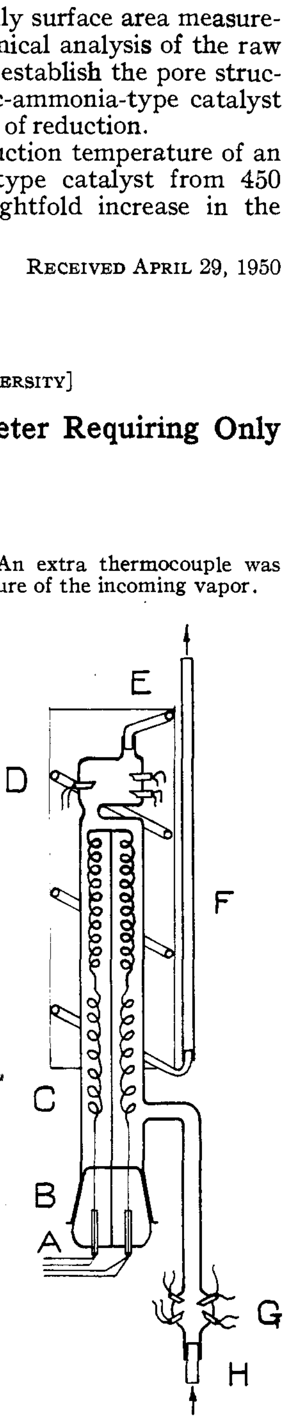

Fig. 1.—Calorimeter assembly.

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(1) This paper is an abstract from the Ph.D. thesis of A. E. Reynolds, whose present address is Hercules Experiment Station, Wilmington, Del.

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