

equations), and the electrophoretic effect has been based on the ion valencies. The assumptions involved here probably give rise to the greatest uncertainties in the calculations. Onsager¹⁹ has shown that in solutions containing more than two ion species, the treatment is more complex than in the case of single electrolytes. However, in dilute solutions the modifications are small, and it is unlikely that the simpler treatment used in the present case is seriously in error. In calculating x , a first value is obtained by taking the ion conductances at zero concentration. Truer values are then quickly obtained by approximations. The final values are given in Table III. The values of the dissociation constant

$$K = \frac{[\text{La}^{3+}][\text{SO}_4^{2-}]f_1f_2}{[\text{LaSO}_4^+]f_3} = \frac{(\frac{1}{3}C - x)(\frac{1}{2}C - x)f_1f_2}{xf_3}$$

where the activity coefficients are obtained from equation (4), are given in the last column of this table. A slight but systematic drift in the figures is probably the result of the approximations

(19) Onsager and Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932)

involved. Extrapolation to zero concentration indicates that the most probable value of K is 2.4×10^{-4} .

Summary

The conductances of sodium and potassium sulfate solutions at 25° have been measured over the range 0.0001 to 0.001 equivalents per liter. From the Owen method¹ of extrapolation, the zero conductance sulfate conductance averages 80.00 ± 0.05 unit. Dissociation constants of the ion-pairs NaSO_4^- and KSO_4^- are found by the method of Davies³ to be 0.19 and 0.11, respectively, and these are shown to predict satisfactorily the transference numbers of these sulfates in dilute solutions.

Lanthanum sulfate conductances in the region 0.0004 to 0.0018 equivalent per liter have been measured at 25°, and the dissociation constant of the ion LaSO_4^+ found to be 2.4×10^{-4} , in good agreement with 2.2×10^{-4} found previously from solubility studies.¹⁷

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RECEIVED JUNE 22, 1949

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

X-Ray Diffraction Studies of the Action of Carbon Monoxide on Cobalt-Thoria-Kieselguhr Catalysts. II

By L. J. E. HOFER,¹ W. C. PEEBLES¹ AND E. H. BEAN¹

Below $235 \pm 10^\circ$ carbon monoxide reacts with finely divided cobalt to form only cobalt carbide²; above this temperature inert free carbon is also formed. This paper presents the results of a study of the reactions occurring above this critical temperature to permit more complete understanding of the problem of free-carbon formation in Fischer-Tropsch catalysts in the synthesis. The formation of such carbon leads to mechanical disintegration of the catalyst³ and to a shift of product distribution toward lighter hydrocarbons, especially methane.⁴ It should be emphasized that these effects are distinct from the inhibiting effect of cobalt carbide on the synthesis.⁵

Experimental

Preparation and Reduction of the Catalyst.—The catalyst, cobalt-thoria-kieselguhr (100:18:100) 108B,^{3,6} the apparatus used for reduction and carburization,³ the X-

ray diffraction apparatus and its operating technique,² the preparation of the gases,² and the general operating procedure³ were the same as those already described in the respective references. Before carburization, all the catalysts were reduced at $400 \pm 2^\circ$ (except that used in experiment 40, which was reduced at $383 \pm 2^\circ$) for 44 to 159 hours to constant weight; the variation in reduction time did not materially affect the course of the subsequent carburization reaction.

Free Carbon and Carbide Carbon Formation between 208 and 298°.—In experiments 23, 24, 27, 31, 33 and 37, the reduced catalyst was carburized with carbon monoxide at various temperatures. After a suitable carburizing period, one of the sample tubes was removed for X-ray diffraction analysis. The remaining sample tubes were then hydrogenated to constant weight at the temperature

TABLE I

CARBON DECOMPOSITION ON COBALT-THORIA-KIESELGUHR CATALYST REDUCED AT 400° IN HYDROGEN

Expt.	Temp. carburization, °C.	Time of carburization, hr.	Diffraction analysis of product	C:Co ratio total	C:Co ^a ratio carbide	C:Co ^b ratio of re-carbided carbon
24	298	62	Dis. cobalt ^c	0.820	0.017	0.008
31	278	15	Dis. Co +	.435	.054	...
23	258	77.8	Co ₂ C	.352	.063	.089
37	243	70.6	Co ₂ C	.138
33	233	112	Co ₂ C	.120	.099	...
27	208	120.8	Co ₂ C	.104	.104	.099

^a Amount of carbon which could be removed by treating with hydrogen at the temperature of carbon deposition. ^b Amount of carbide carbon which could be added by carbon monoxide treatment at 220°. ^c Dis. = disordered.

(1) Research and Development Branch, Office of Synthetic Liquid Fuels, Bureau of Mines, Bruceton, Pa.

(2) L. J. E. Hofer and W. C. Peebles, *THIS JOURNAL*, **69**, 2497 (1947).

(3) Report of the Fuel Research Board for the Year Ended March 31, 1939, H. M. Stationery Office, London, p. 158.

(4) R. B. Anderson, W. Keith Hall, Abraham Krieg and Bernard Seligman, *THIS JOURNAL*, **71**, 183 (1949).

(5) Sol Weller, L. J. E. Hofer and R. B. Anderson, *THIS JOURNAL*, **70**, 799 (1949).

(6) H. H. Storch, *et al.*, Bureau of Mines Technical Paper 709, "Synthetic Liquid Fuels from the Hydrogenation of Carbon Monoxide, Part I."

of the original carburization. Finally, some of the tubes were recarburized to constant weight at 220° (a temperature where only carbidic carbon is deposited). The results of the experiments are summarized in Table I.

The Distinction between Carbidic and Free Carbon.—In this study, four reduced catalysts were carburized at 258° for 122 hours to an average carbon:cobalt weight ratio of 0.2554. Carbon equal to a carbon:cobalt ratio of 0.0841 was removed by hydrogen treatment at 180° to constant weight. After this treatment, the samples were hydrogenated to constant weight at 210° and at successively higher temperatures, as shown in Fig. 2; the length of each hydrogenation varied from 45 to 159 hours.

Inhibition of Carbon Deposition by the Presence of Carbide.—In this study, catalyst 108B was reduced at 383° for 92 hours. The carbide was formed in the catalyst by treatment in a stream of carbon monoxide for 134 hours at $196 \pm 2^\circ$.

Discussion of Results

Free Carbon and Carbidic Carbon Formation between 208° and 298°.—Previous X-ray diffraction studies of the cobalt-thoria-kieselguhr catalyst reduced with hydrogen in the range 350–450° have shown that it has an unusual powder diffraction pattern composed of only three major lines. These can be indexed as the 111, 220 and 311 lines of face-centered cubic (f.c.c.) β -cobalt, but this indexing assumes that for some reason the 200 and 222 lines of β -cobalt do not appear in the pattern. These same three lines can also be indexed as the 002, 110, and 112 lines of hexagonal close-packed (h.c.p.) α -cobalt. This indexing assumes that the 100, 101, 103 and 201 lines of α -cobalt do not appear for some reason. In previous papers,⁵ this anomalous phase has been called β -cobalt since the f.c.c. indexing involved fewer assumptions. It is well-known that the h.c.p. structure of metals can be built up by piling close-packed layers of atoms upon each other in an ABC-ABC... sequence so that corresponding atoms of every third layer are directly above the other. Edwards and Lipson⁷ and Wilson⁸ have observed line broadening of some but not all the lines of massive h.c.p. α -cobalt, and they have attributed this broadening to occasional failure in the ABCABC... sequence. Edwards and Lipson and Wilson have calculated theoretically which lines should be affected by the broadening, and their results indicate that precisely those lines which fail to appear in our cobalt samples are those for which broadening is predicted. Careful examination of the diffraction patterns of these reduced cobalt catalysts reveals very faint traces of 100 and 101 h.c.p. and 200 f.c.c. reflections. Therefore, the cobalt-thoria-kieselguhr catalyst after reduction has a highly disordered layer structure. This is evidence that the goal of the catalyst designers was to achieve the proper particle size upon reduction of the catalyst at the α - β -transition temperature ($\sim 400^\circ$) where the disorder will be maximum.

(7) Edwards and Lipson, *Proc. Roy. Soc. (London)*, **A180**, 268 (1942).

(8) Wilson, *ibid.*, **A180**, 277 (1942).

When cobalt carbide is hydrogenated to the metal at temperatures below 300° normal h. c. p. α -cobalt is formed. This fact is of considerable utility in tracing the origin of cobalt metal in the catalyst.³

The results of experiments showing free carbon and carbidic carbon formation between 208 and 298° are shown in Table I and Fig. 1. The diffraction data of Table I show that the carburized product changes progressively from one containing only cobalt carbide to one containing only disordered cobalt as the carburizing temperature increases from $\sim 243^\circ$ to $\sim 298^\circ$. No h.c.p. α -cobalt was observed. The amount of carbide found at the end of the carburizing period is, therefore, a maximum, because any cobalt carbide decomposing into cobalt metal would have formed α -cobalt and not the disordered form of cobalt.^{5,9}

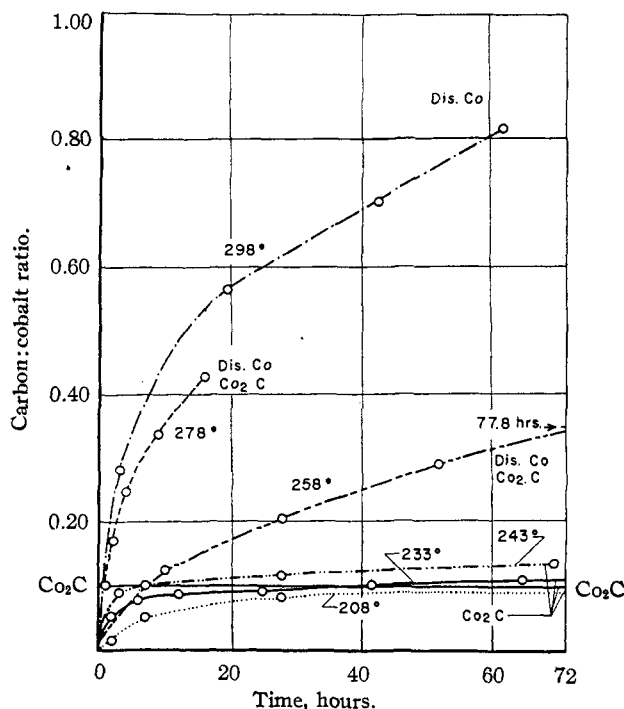


Fig. 1.—Carburization of a cobalt:ThO₃:kieselguhr catalyst with carbon monoxide in the temperature range, 208–298°.

Bahr and Jessen¹⁰ have shown that hydrogen reacts with carbidic carbon in cobalt at temperatures below 300°, forming methane but leaving the free carbon unaffected. Column 6, therefore, is a measure of the carbidic carbon in the carburized product. It will be seen that the amount of carbidic carbon decreases with increasing temperature of carburization. These results parallel the X-ray diffraction data.

In three of the experiments, an attempt was made to recarbide the carburized product after

(9) L. J. E. Hofer, E. M. Cohn and W. C. Peebles, *J. Phys. and Colloid. Chem.*, **53**, 661 (1949).

(10) H. A. Bahr and V. Jessen, *Ber.*, **68**, 2226 (1930).

hydrogen treatment. The results are shown in column 7. Carbide carbon roughly equal to that which had been removed by hydrogenation was all that could be introduced at 220°. This may be interpreted to mean that the free carbon has made certain portions of the catalyst inaccessible to carbiding either by poisoning or by mechanical blocking. In experiment 24, almost the entire catalyst was so blocked.

Hydrogenation at 208° for ninety hours of three samples which had been carburized at 298° for two hours, twenty-three hours, and forty-five and one-half hours, respectively, showed that the maximum carbide content (about 0.02 carbon:cobalt ratio) was achieved after only two hours, when the total carbon:cobalt ratio was about 0.18. Thus, the factor which inhibits carbide formation becomes important when only a relatively small amount of free carbon has been formed. Presumably, at temperatures intermediate between 298 and 243°, somewhat more time will be required to achieve maximum carbide content.

The Distinction between Carbide and Free Carbon.—To determine whether the relationship between the reactivity of free carbon and of carbide carbon is the same in a carburized cobalt-thoria-kieselguhr catalyst as it is in the carburized massive-cobalt samples used by Bahr and Jessen,¹⁰ a reduced cobalt-thoria-kieselguhr catalyst was carburized under conditions leading

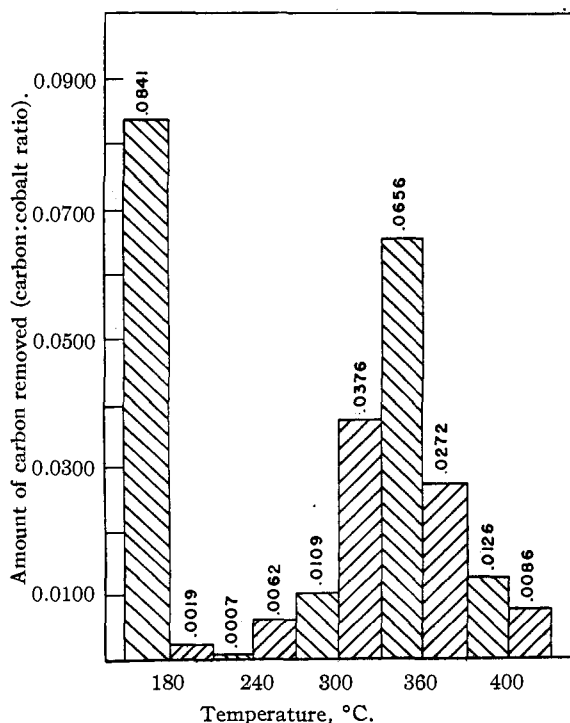


Fig. 2.—Carbon removed by hydrogenation at increasing temperatures showing the distinction between free carbon and carbide carbon.

to large amounts of both carbide and free carbon. This catalyst was then treated with hydrogen at a series of successively higher temperatures 30° apart, beginning with 180°. At each temperature, the hydrogen treatment was continued until constant catalyst weight was reached. The amounts of carbon so removed are represented in the histogram in Fig. 2. The height of each bar in this histogram represents the fraction of carbon reactive to hydrogen in the temperature range indicated. It will be noted that the carbon falls into two distinct classes of reactivity: (a) That carbon which is reactive below ~210–240° and (b) that which is reactive only above this temperature range (free carbon). [This range is somewhat lower than that of 270–300°, which can be deduced from the data of Bahr and Jessen.] The present experiment suggests that a considerable amount of the carbon deposited in experiment 24 would be converted to methane at 298°. As this is not the case, we must postulate that the reactivity of the free carbon decreases with increase in the temperature at which it is formed.

Carbon Deposition on a Fully Carbided Catalyst Compared with that on a Reduced Catalyst.—It has been suggested that free-carbon deposition proceeds by way of carbide as an intermediate.¹¹ To get more information on the effect of carbide on free-carbon deposition, two samples of 108B catalyst, identical in all respects except that the cobalt in one was converted to Co_2C , were carburized at $285 \pm 2^\circ$ for twenty-two hours. The results are shown in Fig. 3, and indicate that carbon deposition initially is about twenty times faster on the metallic catalyst than on the carbided catalyst. During the twenty-two hours of carburization, the rate of carbon deposition on the (originally) metallic catalyst de-

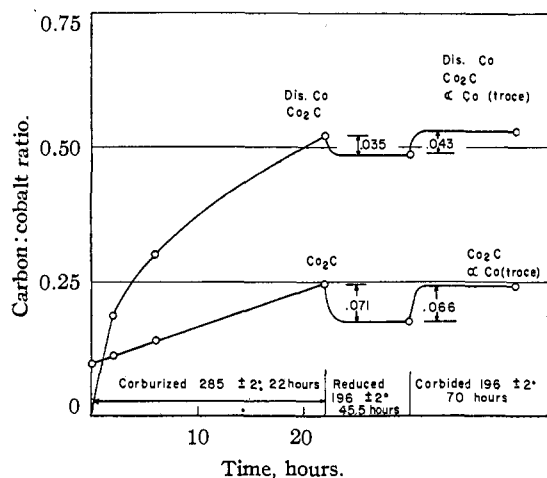


Fig. 3.—Comparison of carbon deposition on a carbided catalyst with carbon deposition on an uncarbided one.

(11) F. Fischer and H. A. Bahr, *Gesam. Abhandl. Kenntnis der Kohle.*, 8, 255 (1929).

creased greatly. On the other hand, the carbon-deposition rate remained essentially constant during the same period on the carbided catalyst. X-Ray diffraction analysis of samples which had received essentially parallel treatment up to the point indicated on the curve are also shown in Fig. 3. The precarbided catalyst contained only Co_2C , showing that no net change in carbide content had taken place. The rate of carbon deposition on the precarbided sample was 0.0064 g. carbon/g. cobalt/hour, and the rate of decomposition of carbide in this same catalyst was calculated by means of the activation energy and rate constants previously determined⁹ to be 0.0015 g. carbon/g. cobalt/hour. Thus, it is interesting to note that the rate of carbon deposition is of the same order of magnitude (though higher by a factor of 4) as the rate of carbide decomposition. The X-ray diffraction analysis of the initially uncarbided sample after

twenty-two hours showed only disordered cobalt plus a small amount of Co_2C . On hydrogenation at 196° , the initially carbided sample lost carbon equal to a carbon : cobalt ratio of 0.071. On recarbiding at 196° , a nearly equal amount of carbon (0.066) was replaced.

Summary

1. Reduced cobalt-thoria-kieselguhr catalysts produced increasing amounts of free carbon and decreasing amounts of cobalt carbide on carburization with carbon monoxide at increasing temperatures in the range 243 to 298° . At the high temperatures, the maximum amount of carbide is formed within the first five hours of carburization.

2. Free carbon tends to make the catalyst inaccessible to further carbide formation.

3. Carbide inhibits free-carbon deposition.

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RECEIVED DECEMBER 2, 1949

[CONTRIBUTION NO. 1350 FROM THE GATES AND CRELLIN LABORATORY OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

The Crystal Structure of 2,2'-Diiododiethyltrisulfide

By JERRY DONOHUE

An investigation of the crystal structure of 2,2'-diiododiethyltrisulfide (Fig. 1) was recently carried out by Dawson and Robertson¹ (hereinafter referred to as D. and R.) who found that crystals of this substance are isomorphous with the space group $D_4^2 - P4_12_1$, and that four molecules are present in the unit cell, which has $a_0 = 6.01 \text{ \AA}$. and $c_0 = 29.4 \text{ \AA}$. Since the general position of this space group is eight-fold, it follows that each molecule has point symmetry $C_2 - 2$, a fact which eliminates the possibility that this trisulfide has the thiodisulfide structure,

S
|
R-S-S-R,
leaving only the straight-chain structure, R-S-S-S-R, and the dithiosulfone structure,

S
|
R-S-R,
|
S

to be considered. Fourier analysis of the ($h0l$) data led to the determination of the parameters for the sulfur and iodine atoms, and to the assignment of the straight-chain structure to molecules of 2,2'-diiododiethyltrisulfide.

This conclusion is an agreement with the previous results of Donohue and Schomaker, who assigned the straight-chain structure to the compound dimethyltrisulfide on the basis of an electron diffraction investigation.²

Because of the small fraction which the carbon atoms contribute to the total scattering D. and

R. made no attempt to locate these atoms in their electron density plots, but merely assigned to them parameters which "were probable values only, based on the requirements of accepted single bond lengths and angles for the atoms in question." These parameters were not used to calculate the contributions the carbon atoms make to the ($h0l$) reflections—the calculated values of F_{h0l} which were used in the final comparison with the observed values of F_{h0l} included sulfur and iodine scattering only. Nevertheless, they discussed in some detail the shape of the molecule, in particular, pointing out that the group $\text{S}_1-\text{S}_2-\text{S}_1-\text{C}_2$ was very nearly coplanar and *trans*, that the group $\text{S}_2-\text{S}_1-\text{C}_2-\text{C}_1$ was also *trans* and not quite coplanar, and that the group $\text{S}_1-\text{C}_2-\text{C}_1-\text{I}$ had a configuration obtained by a rotation about the C_2-C_1 bond of approximately 90° from a coplanar *trans* configuration. It should be remembered, however, that this discussion is based wholly on positions of the carbon atoms for which no evidence was found by D. and R. in their electron density maps.

The coplanar *trans*- configuration suggested for the $\text{S}-\text{S}-\text{S}-\text{C}$ group is not in agreement with the configuration found by Donohue and Schomaker² for dimethyltrisulfide: their data suggest a dihedral angle between the planes $\text{S}-\text{S}-\text{S}$ and $\text{S}-\text{S}-\text{C}$ of slightly greater than 90° .³ Moreover,

(3) A recalculation of the dihedral angle in dimethyltrisulfide gives the value 93° . This calculation is based on the value of 4.0 \AA . for the long $\text{C} \dots \text{S}$ distance as indicated by the radial distribution function, and on the final values for the other structural parameters, which were determined by the correlation treatment. The published

(1) I. M. Dawson and J. M. Robertson, *J. Chem. Soc.*, 1256 (1948).

(2) J. Donohue and V. Schomaker, *J. Chem. Phys.*, **16**, 92 (1948).