ion method; 45.7 calcd. Mol. wt. (Dumas) 160 at 129° and 152 at 190°, indicating more than usual deviation from the ideal gas law; 127 calcd. and 129–135 could be expected.

Discussion

1. The known phosphorus mixed halides now include six stable compounds (difluorochloride,[7] fluorodichloride,[7] fluorodibromide,[7] fluorodiisocyanate, difluoroisothiocyanate, dichloroisocyanate), two less stable ones (chlorodiisocyanate, dichloroisothiocyanate) and two rather unstable compounds (difluorobromide,[7] difluorosiocyanate). In the related silicon series the trifluoroisocyanate is rather unstable, although the trifluorobromide is stable.

2. The existence of phosphorus difluoroisothiocyanate, as the only member of its series, is in agreement with previous preparations. Recalculation of data of Dixon and Taylor[8] by the N^2 formula gives the molar refraction of phosphorus isothiocyanate as 54.52 ml.; this yields (—NCS) = 15.40 ml., clearly in the isothiocyanate range.[9] The value of 25.66 ml. found compares favorably with the value of 25.72 ml. calculated for the difluoroisothiocyanate.

3. Vitrification appears to be rather usual among compounds of this general type,[3] having been noted among: $POCl_2(NCS)$, $PCl_2(NCO)$, $PCl(NCO)_2$, $PF_2(NCS)$ and $SiCl_3(NCS)$—the structural formula of the last is subject to verification.

4. The boiling points of the phosphorus fluoroisocyanates—and also those of the silicon fluoroisocyanates—are an average of 21° higher than those predicted by linear interpolation between the boiling points of the appropriate two binary halides (difluoro-, b. p. −11°; monofluoro-, b. p. 79° expected). An unexpectedly high boiling point of phosphorus difluoroisothiocyanate (90° instead of 21° as calculated) recalls the unexpectedly high boiling points of monohalo silanes, such as the chloride and bromide.

Acknowledgments.—The author thanks Professor George S. Forbes of this Laboratory for helpful suggestions.

Summary

1. Phosphorus isocyanate and antimony trifluoride react without a catalyst yielding both phosphorus fluoroisocyanates; the difluoro member is best prepared from the monofluoro derivative. Phosphorus fluorodiisocyanate, $PF(NCO)_2$, b. p. 98.7°, is quite stable at room temperature. Phosphorus difluoroisocyanate, $PF_2(NCO)$, decomposes rapidly enough at a b. p. of 12° to limit the purification attainable by distillation; this instability is comparable with that of the previously known silicon trifluoroisocyanate and of phosphorus difluorobromide.

2. Phosphorus isothiocyanate and antimony trifluoride yield only one mixed halide, phosphorus difluoroisothiocyanate, $PF_2(NCS)$, b. p. 90.3°, which shows no decomposition in distillation at 760 mm.

Thermal decomposition of black polymeric phosphorus isothiocyanate yields carbon disulfide.

3. Miscibilities of the three new compounds with carbon disulfide have been studied. Several physical properties have been measured.

CAMBRIDGE, MASSACHUSETTS

RECEIVED FEBRUARY 10, 1947

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[7] Booth and Bozarth, THIS JOURNAL, **61**, 2927 (1939); Booth and Frary, *ibid.*, **61**, 2934 (1939).

[8] Dixon and Taylor, *J. Chem. Soc.*, **93**, 2148 (1980).

[9] Delépine, *Ann. chim.*, [8] **25**, 557 (1912).

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

X-Ray Diffraction Studies of the Action of Carbon Monoxide on Cobalt-Thoria-Kieselguhr Catalysts. I[1]

BY L. J. E. HOFER[2] AND W. C. PEEBLES[3]

Finely divided cobalt metal and carbon monoxide react to form a product whose composition corresponds to Co_2C.[4] This reaction occurs under conditions of temperature and pressure which do not differ materially from those of the Fischer–Tropsch reaction on cobalt catalysts. Recently this product was found to be a distinct new carbide with a characteristic crystal structure of its own.[5] The carbon in this carbide is very easily converted to methane by the action of hydrogen at 250°, in contrast to the inertness of the carbon formed on cobalt by carbon monoxide at temperatures above 250°. The genesis as well as the characteristics of this carbide suggest that it may be either an intermediate in the Fischer–Tropsch reaction or the crystalline phase whose surface catalyzes the reaction. The chemical and physical behavior of this carbide, especially its formation by carbon monoxide and its destruction by hydrogen, is of fundamental importance to the understanding of the mechanism of the Fischer–Tropsch reaction.

Previous studies of the carburization of cobalt–thoria–kieselguhr catalysts and of the hydrogenation of such carburized catalysts showed that both

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[3] Physicist, Central Experiment Station, Bureau of Mines, Pittsburgh, Pa.

[4] H. Bahr and V. Jessen, *Ber.*, **63**, 2226 (1930).

[5] L. J. E. Hofer and W. C. Peebles, THIS JOURNAL, **69**, 893 (1947).

reactions were much more rapid for the catalyst[6,7] than for free cobalt.[4] This might be the result of an increase in surface area of the cobalt when it is associated with thoria and kieselguhr. On the other hand, preliminary X-ray diffraction studies of catalysts reduced with hydrogen at 400° showed that these catalysts all contained face-centered cubic β-cobalt. This observation is in accord with that of Emmett and Schultz[8] that the transition from β-cobalt to hexagonal, close-packed α-cobalt lies between 340 and 380° and is very sluggish. At the temperature of synthesis (170–210°), β-cobalt is metastable. The difference in the behavior of the catalyst as compared with pure cobalt may thus be due to the difference in the crystal structures involved. In the present paper, this and related questions are discussed.

Experimental

Two types of catalysts were studied. Catalyst 108B, a precipitated cobalt–thoria–kieselguhr (100:18:100) preparation, was made essentially according to the directions of Fischer and Koch[9]; catalyst 89K, a precipitated cobalt–thoria–magnesia–kieselguhr catalyst (100:6:12:200), was made according to the directions of Hall.[10] A more complete description of the preparation and properties of these catalysts will soon be published.[11] Catalyst 108B was deposited on Johns–Manville Filter-Cel, 89K on a Portuguese kieselguhr.[12] Activity tests showed that both of these catalysts were quite active; catalyst 108B produced 97 g. and 89K, 103 g. of liquid hydrocarbons per cubic meter of synthesis gas ($1CO + 2H_2$) at 100 p. s. i., respectively. The catalysts were pressed into pellets 0.125 inch in diameter and about 0.1 inch high, with a bulk density of 1.23 g. per cubic cm. (Preliminary experiments showed that carburization proceeded as rapidly in these pellets as in a powder made from these pellets.)

The apparatus, preparation of gases, and general procedure were similar to those previously described in the study of the carburization of pure cobalt metal.[5] Four 4-g. samples of catalyst were weighed out into individual reaction vessels for each experiment. The reaction vessels were then placed side by side in an aluminum-block furnace, and the catalyst was reduced *in situ* by a stream of hydrogen flowing initially at 5 and later at 0.9 liter per hour. During reduction the temperature was gradually raised to 398 ± 2° and maintained at this temperature until the reaction vessels had attained constant weight. (The reduction periods at 398° were 61, 42, and 84 hours for experiments 13, 25, and 27, respectively. These relatively long reduction periods were found necessary in order to achieve quantitative reduction. Activity tests proved that catalysts reduced by this procedure were still quite active.) Reduction of the raw catalysts was much more difficult than the reduction of pure cobalt oxide.[5] During reduction, the color of the catalyst changed from brownish-gray to black.

In removing samples for X-ray analysis, the reaction vessels were opened in an atmosphere of carbon dioxide and the contents were dropped in a beaker of petroleum ether. The catalyst, wet with petroleum ether, was ground to a fine paste, mixed with collodion, and partly extruded from a section of stainless steel tubing. This procedure prevented oxidation of the reduced or carburized catalysts, which otherwise tend to be pyrophoric. 19-gage tubing of 0.7 mm. inside diameter was used. The specimens were mounted in a Debye–Scherrer camera of 71.62 mm. inside diameter. Fe $K\alpha$ radiation, as obtained from a sealed-off X-ray tube equipped with beryllium windows, and manganese filters was used.

The data plotted in Figs. 1, 2 and 3 represent the ratio of carbon deposited to the amount of cobalt in the catalyst. Each point represents the average of the results on four reaction vessels, except where one or more of the reaction vessels has been removed for X-ray analysis. In these cases, an uncorrected average of the results for the remaining reaction vessels may produce an apparent discontinuity in the curve. In the experiments represented by Figs. 1 and 2, this made little difference so the uncorrected average was used. However, in the experiment represented by Fig. 3, the simple average was corrected to avoid discrepancies of the order of 5%.

Results and Discussion

Raw and Reduced Catalysts.—The raw catalysts, both 108B (Fischer) and 89K (Hall), were almost completely amorphous to X-rays. The original kieselguhrs were also almost entirely amorphous to X-rays, although the Johns–Manville Filter-Cel has a distinct line corresponding to a Bragg spacing of 3.35 Å. A sample of thoria precipitated in the same manner as catalyst 89K was also completely amorphous. After these catalysts were heated for three hours at 450° in air, their diffraction patterns distinctly showed all the lines of Co_3O_4 (isomorph of magnetite), but the thoria and kieselguhr were revealed only by a heavy background. Exposure of individual kieselguhrs and the thoria to the same conditions left them still amorphous. The cobalt in the catalyst can thus undergo solid-phase reactions in which the thoria and kieselguhr do not participate to any great extent.

The diffraction patterns of reduced catalysts reveal the lines of a phase that is apparently face-centered cubic β-cobalt. The lines are diffuse and superimposed on the heavy background of the amorphous thoria and kieselguhr; the line broadening corresponds to crystallites about 200 Å. in diameter. The reflections from the 200 planes and the 222 planes are considerably weaker than reported in the literature.[13] The lattice parameter, as determined by the modification of the method of Davy[14] previously described[5] is 3.539 ± 0.003 Å. This is in excellent agreement with the value of 3.545 ± 0.005 Å. given in the review of Neuberger.[15] X-Ray diffraction patterns of partly reduced catalysts fail to show the lines of β-cobalt, this is undoubtedly due to the obscuring of the reflections by the background

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[6] Ya. T. Eidus and N. D. Zelinskiĭ, *Bull. acad. sci. U. R. S. S.*, 45 (1942) (Survey of Foreign Petroleum Literature, U. O. P. Trans. 376).

[7] S. R. Craxford and E. K. Rideal, *J. Chem. Soc.*, II, 1604 (1939).

[8] P. H. Emmett and J. F. Schultz, THIS JOURNAL, **51**, 3246 (1929).

[9] F. Fischer and H. Koch, *Brenn. Chem.*, **13**, 61 (1932).

[10] C. C. Hall, *J. Soc. Chem. Ind.*, **65**, 128 (1946).

[11] H. H. Storch, *et al.*, Bureau of Mines Technical Paper 709; Synthetic Liquid Fuels Process. Hydrogenation of Carbon Monoxide. Part I, in press.

[12] Obtained through the courtesy of C. C. Hall of the British Fuel Research Station.

[13] Data Cards for the Identification of Crystalline Materials by the Hanawalt X-ray Diffraction Method, Am. Soc. for Testing Materials, Philadelphia, Pa.

[14] W. P. Davy, "A Study of Crystal Structure and Its Application," McGraw-Hill Book Co., New York, N. Y., 1934, p. 163.

[15] M. C. Neuberger, *Z. Krist.*, **93**, 1 (1936).

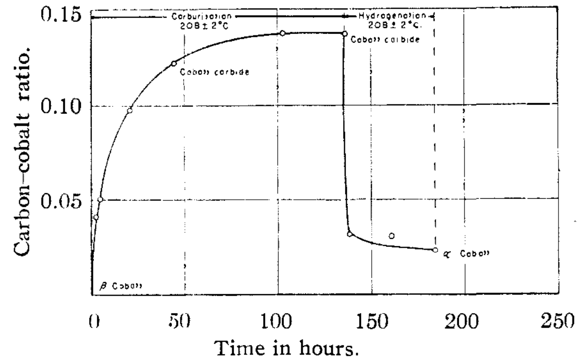

Fig. 1.—Carburization of 100:6:12:200 cobalt–thoria–magnesia–kieselguhr catalyst (89-K) and its subsequent hydrogenation at 210°.

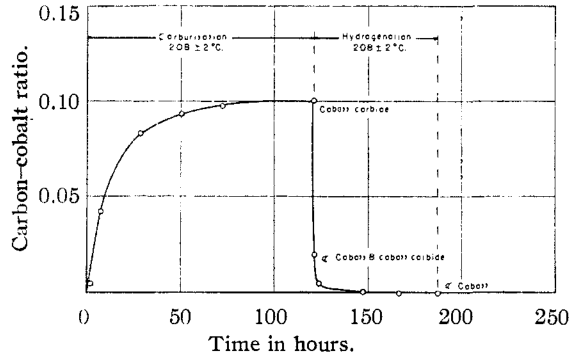

Fig. 2.—Carburization of 100:18:100 cobalt–thoria–kieselguhr catalyst (108-B) and its subsequent hydrogenation.

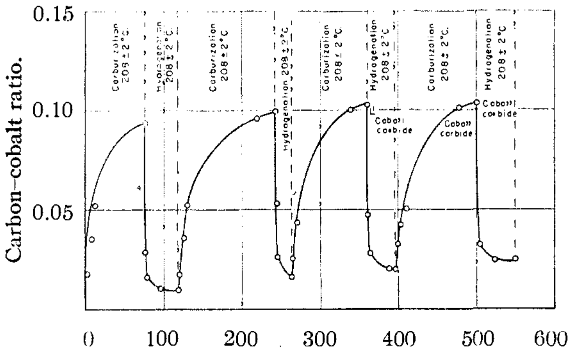

Fig. 3.—Successive cycles of carburization and hydrogenation of a 100:18:100 cobalt–thoria–kieselguhr catalyst 108 B at 210°.

previously mentioned. The diffraction data on the reduced β-cobalt are shown in Table I.

Carbide Formation and Hydrogenation of the Carbide.—As in the case of pure hexagonal α-cobalt, the amount of carbon deposited approaches a definite limit. X-Ray diffraction patterns taken during this process (Fig. 4) show that it corresponds to the development of a new phase at the expense of the original β-cobalt. The interplanar spacings for which Bragg reflections occur are identical with those found in the cobalt carbide prepared by carburizing pure hexagonal α-cobalt.[5] When complete carburization has taken place (as shown by no further gain in weight of the reaction tubes), no trace of β-cobalt can be detected. The only Bragg spacings of the carbide which cannot be found in the patterns from the carburized catalyst are reflections that were reported as very weak or doubtful (due to coincidence with α-cobalt lines). The lines are not as sharp as those reported for the pure cobalt carbide, and there is a heavy background, as is the case for all these catalysts. The results of the X-ray diffraction analyses are placed on the curves of Figs. 1, 2 and 3 at the points where the corresponding samples were taken.

TABLE I

X-RAY DIFFRACTION DATA FOR FACE-CENTERED CUBIC COBALT AS FOUND IN CATALYST 108B ON REDUCTION

hkl	Relative intensity Obs.	Relative intensity Hanawalt	Observed average of two films	Calculated[a] $a_0 = 3.545$ Å. (Neuberger)
111	S	1.00	2.0409	2.0467
200	vw	0.44		1.7725
220	M	.22	1.2554	1.2533
311	S	.22	1.0647	1.0688
222	vw	.05		1.0233

[a] Observed a_0 = 3.539 Å.

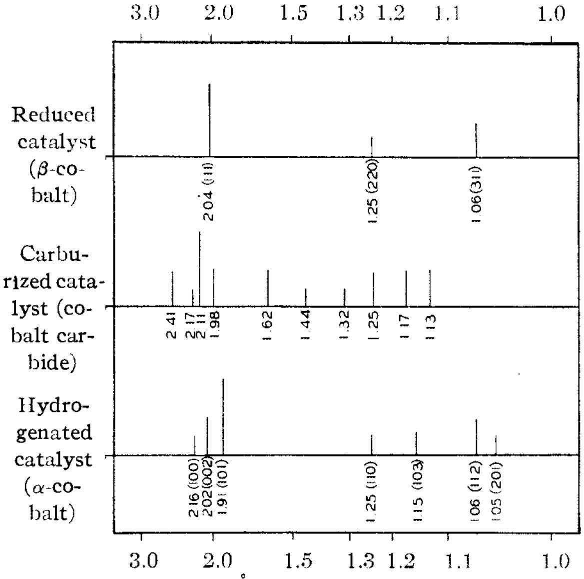

Fig. 4.—X-Ray diffraction patterns of catalyst 89K 100:6:12:200 cobalt–thoria–magnesia–kieselguhr taken at various stages of treatment with carbon monoxide and hydrogen.

Catalyst 89K (Hall catalyst) and catalyst 108B (Fischer catalyst) were carburized at 208 ± 2° with carbon monoxide flowing at the rate of 0.25 liter per hour. Under these conditions, the rates of carburization were much more rapid on 89K than on 108B, the values being 0.0205 and 0.0025

g. carbon per gram cobalt per hour, respectively. The carbon–cobalt ratio for 108B approached asymptotically a value close to the theoretical for Co_2C (0.1015), while for 89K it approached 0.137. The difference between the two experiments may result from free carbon formation during the rapid initial stage of the reaction on catalyst 89K.

Treatment with hydrogen at 208 ± 2° with a flow rate of 0.6 liter per hour rapidly removed the carbidic carbon as methane. X-Ray diffraction patterns proved that the cobalt carbide was converted to the stable α-cobalt. Thus, the metastable β-cobalt can be converted to the stable α-cobalt by way of cobalt carbide at a temperature more than 100° below the transition temperature (340–380°). Other experiments show that the β-cobalt in a reduced 108B catalyst can withstand at least a week of exposure to temperatures as high as 300° without becoming converted to α-cobalt. In the case of the 89K catalyst, not all the carbon deposited during hydrogenation was removed. This supports the conclusion that free carbon was deposited on this catalyst. Moreover, the ratio of the easily removable carbon to the available cobalt corresponds closely to the formula Co_2C.

Figures 1 and 2 both show that the rate of formation of cobalt carbide is much slower than the rate of its hydrogenation. In order to determine whether α-cobalt and β-cobalt as formed react in the same way with carbon monoxide, reduced samples of catalyst 108B were carburized and the carburized samples hydrogenated, these steps being repeated several times. The results are presented in Fig. 3. After the first cycle, the cobalt is in the α-form, but the subsequent cycles were not noticeably different from the first cycle; thus α- and β-cobalt react with carbon monoxide in nearly the same way.

Acknowledgment.—The authors wish to thank Dr. R. B. Anderson, who directed the operation of the catalyst testing, Mrs. Norma Golumbic, who prepared the catalysts, and all the personnel, who operated the catalyst testing units for the catalysts and activity data.

Summary

1. Reduction of the Fischer– and Hall-type Fischer–Tropsch catalysts at 400° leaves the cobalt in the face-centered cubic (β) form which does not convert readily to the hexagonal close-packed (α) form.

2. On carburization of the reduced catalyst, the cobalt is converted to the same carbide previously reported by the authors.[5]

3. The carburization of α-cobalt and β-cobalt as associated with kieselguhr, thoria, and magnesia proceeds at nearly the same rates and results in the same crystalline carbide.

4. Hydrogenation of the carbide forms methane and the stable α-cobalt.

5. The cycle of carbiding the cobalt in the reduced catalyst and hydrogenating the carbide so formed can be repeated apparently indefinitely at 210°.

PITTSBURGH, PA. RECEIVED APRIL 14, 1947

[CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY]

The Formation of Uranium Hydride[1]

BY JOSEPH E. BURKE[2] AND CYRIL STANLEY SMITH[2]

When massive metallic uranium is heated in an atmosphere of hydrogen, uranium hydride is formed and spalls off continuously as an exceedingly fine, gray, highly pyrophoric powder, the maximum particle size of which is 4 to 5 microns. Prior to the war, the compound had been reported only by Driggs,[3] who gave methods for its preparation, and assigned the formula UH_4. During the war several workers[4] studied the compound under the auspices of the Manhattan District. It is the object of this report to describe the effect of reaction temperature and hydrogen purity on the rate of formation of the compound, and to present the results of a new determination of its formula.

Experimental Procedure

For most of the work, 0.5-g. pieces of $^1/_{16}$ inch uranium metal wire of about 99.9% purity were used as starting material. The reaction proceeds in an identical fashion with much larger pieces. The weighed piece of the wire was contained in a Pyrex bulb which was connected to an all-glass gas train. The bulb was evacuated, and then heated to the desired reaction temperature in an accurately controlled electric furnace; hydrogen was then admitted, and both the rate of gas absorption and the total amount of gas absorbed were measured with a gas buret. The total volume of the reaction bulb, gas buret, and connecting lines was about 200 cc. All measurements were made at atmospheric pressure (585 mm. at Los Alamos), and the final measurement of the total amount of gas absorbed was made with the whole apparatus at room temperature.

In the investigations on the effect of hydrogen purity on the reaction, hydrogen was used (1) directly from the

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[1] This work was carried out under contract between the University of California, and the Manhattan District, Corps of Engineers, War Department. The original report to the Manhattan District is dated November 13, 1943.

[2] Present address: Institute for the Study of Metals, University of Chicago, Chicago 37, Illinois.

[3] U. S. Patents 1,816,830 (1929) and 1,835,024 (1929).

[4] Uranium hydride was first studied on the Manhattan District Project by F. H. Spedding and co-workers at Iowa State College, Ames, Iowa. This work is summarized in reports CC-580 by Spedding, Warf, Newton, Butler, Ayres and Johns, dated April, 1943, and CC-1201, by Spedding, Newton, Warf, Johnson and Nottorf, dated January, 1944. Some of this work has been submitted for declassification and will be submitted to the *Journal of the American Chemical Society* in the near future.