nism of the normal emulsion polymerization reaction needs revision.

Using the data of Tables II and Fig. 4, it is also possible to test the prediction of expression (8) that at a given persulfate concentration the rate of polymerization should be proportional to the reciprocal of the concentration of retarder at large concentrations of retarder. It is seen from Fig. 11 that this is actually the case at three different persulfate concentrations.

3. Assuming the rate of disappearance of *m*-dinitrobenzene to be constant during polymerization, we find (see Table IV) that this rate is 0.071 millimole per hour per liter of aqueous phase. In a subsequent paper, dealing with the behavior of inhibitors, it will be shown that the rate of disappearance of the ideal inhibitor *p*-benzoquinone is 0.057 millimole per hour per liter of aqueous phase in the same recipe. There is evidence, which is not conclusive, that each molecule of *p*-benzoquinone reacts with two monomer free radicals, but that this substance does not copolymerize with the styrene to any appreciable extent under the conditions of our experiments. Since the rate of disappearance of *m*-dinitrobenzene is about the same as that of *p*-benzoquinone, it is evident that *m*-dinitrobenzene does not copolymerize with styrene, and that the adduct formed by addition of the growing polymer chain to the retarder molecule is incapable of reacting with monomer.

4. From the fact that the induction period caused by oxygen is not affected by the presence of *m*-dinitrobenzene, it is evident that this substance has no retarding effect on the copolymerization of oxygen with styrene. Apparently, *m*-dinitrobenzene cannot compete effectively with oxygen for monomer free radicals, nor with monomer for the peroxide free radicals formed by reaction of monomer radicals with oxygen.

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Summary

An experimental study has been made of the effect of retarders on the emulsion polymerization of styrene with potassium persulfate as catalyst. It is postulated that in the presence of large concentrations of a retarder, such as *m*-dinitrobenzene, the rate of polymerization should be given by

$$-\frac{dM}{dt} = K\frac{(C)^n}{(r)} \quad (n = 1)$$

where (C) = concentration of catalyst
(r) = concentration of retarder

The value $n = 1$ has been approached but not attained.

m-Dinitrobenzene is nearly equally effective as a retarder in alkaline and acid recipes. It acts as a chain-breaker and reduces the molecular weight of the polymer formed. From its rate of disappearance, it is concluded that it does not act as a comonomer, but that it reacts with growing polymer chains to produce adduct radicals incapable of further chain propagation.

3,5-Dinitrobenzoate is a very ineffective retarder at a *p*H of 10, but the free acid becomes equal in effectiveness to *m*-dinitrobenzene at a *p*H of 1. The behavior of water-soluble and oil-soluble retarders is explained on the basis of the loci of the activation and propagation reactions.

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

The Role of Bulk Cobalt Carbide in the Fischer–Tropsch Synthesis[1]

BY SOL WELLER,[2] L. J. E. HOFER[2] AND R. B. ANDERSON[2]

The Fischer–Tropsch synthesis involves formation of hydrocarbons by the passage of carbon monoxide–hydrogen mixtures over metallic catalysts, usually cobalt or iron, at elevated temperatures. With cobalt catalysts, the equation for the reaction may be written approximately as

$$xCO + 2xH_2 = (CH_2)_x + xH_2O$$

The hypothesis that the synthesis proceeds through the intermediate formation of a metal carbide was first suggested by Fischer and Tropsch[3] in 1926. It has been popular ever since in the scientific and the technical literature[4]; patents have even been granted based on the idea that carbiding of catalysts before synthesis is desirable.[5]

The concept of metal carbide as a synthesis intermediate has heretofore been used rather loosely. Distinction has rarely been made between bulk carbide and some sort of "surface" carbide as a possible intermediate. Craxford and Rideal,[4] for example, have done some of the important work on the mechanism of the synthesis and speak of "surface" carbide; they give as evidence for the carbide theory, however, only examples indi-

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(3) Fischer and Tropsch, *Brennstoff Chem.*, **7**, 97 (1926).

(4) For example, Craxford and Rideal, *J. Chem. Soc.*, 1604 (1939); Eĭdus, *Bull. Acad. Sci. URSS*, 447 (1946).

(5) Elian, U. S. Patent 2,369,548; Atwell, U. S. Patent 2,409,235.

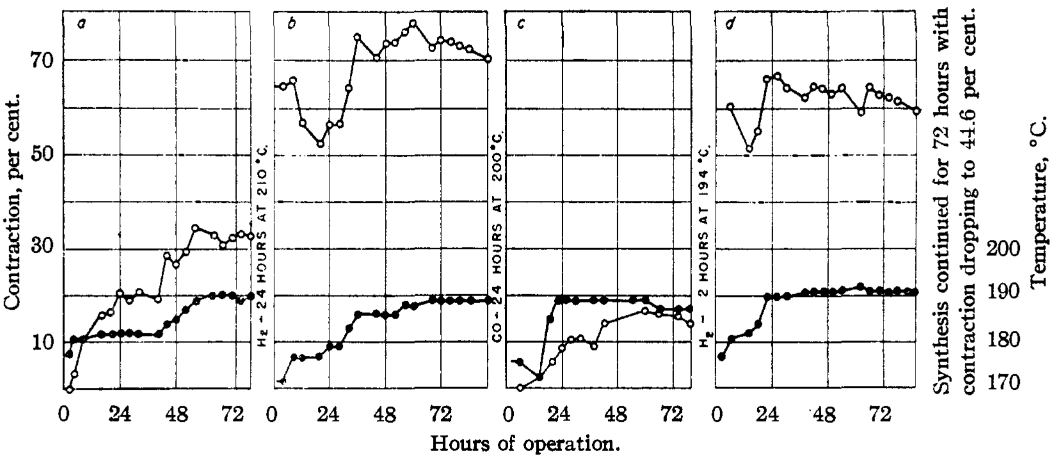

Fig. 1.—Apparent contraction ○ and temperature of operation ● *versus* time for test 73 with cobalt catalyst 108 B at atmospheric pressure. Catalyst was reduced in hydrogen at 360° and carbided with carbon monoxide at 200° for twenty-four hours prior to testing.

cating that bulk carbide accumulates in the catalyst under some conditions. The idea of "surface" carbide is a particularly elusive one, since it is very difficult to distinguish between a "surface" carbide and adsorbed carbon monoxide. The role of "surface" carbide as an intermediate in the synthesis will not be discussed here, but evidence will be presented which demonstrates that bulk carbide, in the case of cobalt catalysts, probably is neither an intermediate in the synthesis nor a catalytically active substrate for the synthesis.

Results and Discussion

Inhibition of Synthesis.—The presence of extensive amounts of carbide in cobalt catalysts severely inhibits the Fischer–Tropsch synthesis. In one experiment, for example, a cobalt–thoria–magnesia–kieselguhr (100:6:12:200) catalyst[6] was reduced with hydrogen at 400°, and carbided with carbon monoxide for twenty hours at 200°; the volume of carbon monoxide reacted was equivalent to 70% conversion of the cobalt to Co_2C. (Treatments of catalysts with hydrogen, carbon monoxide, and synthesis gas were carried out at atmospheric pressure.) Exposure of this carbided sample to circulating synthesis gas resulted in an over-all synthesis rate at 150° of 60–70 × 10^{-4} g. C/g. Co/hour. After removal of the carbide by hydrogenation at 150–194° and re-exposure of the sample to synthesis gas, a synthesis rate of 250–300 × 10^{-4} g. C/g. Co/hour was observed—an increase of 400%. The distribution of the synthesis products was about the same in both cases.

In another experiment, a sample of cobalt–thoria–kieselguhr (100:18:100) catalyst[7] was carbided in carbon monoxide at 210° to an extent equivalent to 110% Co_2C.[8] This sample was observed to have no appreciable activity in flowing synthesis gas, while a control sample, similarly reduced initially but not carbided, gave copious yields of oil and water. Partial hydrogenation of the carbided sample at 190°, with removal of 72% of the carbon which had been introduced, restored the activity to about one-half the normal value.

The loss of synthesis activity on carbiding can persist even when synthesis is continued for several days. This behavior is illustrated in Fig. 1. A sample of cobalt–thoria–kieselguhr catalyst[7] was carbided for 24 hours at 200° after initial reduction. On exposure to flowing synthesis gas at 182°, the carbided sample originally showed no catalytic activity, as measured by the fractional decrease in gas volume (contraction) as the gas passed through the converter (Fig. 1a). During operation for one day at 182°, the contraction rose to 20% but did not increase further during another eighteen hours of synthesis. Increasing the temperature to 190° increased the contraction only to 33%, even after a day. Subsequent hydrogenation of this sample at 210° and re-exposure to synthesis gas resulted in a (normal) contraction greater than 70% at 189° (Fig. 1b). Recarbiding the active catalyst for 24 hours at 200° again reduced the activity to the low value observed after the first carbiding (Fig. 1c) and rehydrogenation of the carbided sample again restored the normal activity (Fig. 1d).

This inhibitory effect of precarbiding before synthesis is not explainable as a poisoning due to free carbon deposited during the carbiding, since the effect is completely reversed by hydrogenation at temperatures where free carbon is not affected.[9] It is also known that carbiding of cobalt catalysts

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(6) Catalyst 89J. Its preparation is described in U. S. Bureau of Mines Technical Paper 709, in press: H. H. Storch, *et al.*, "Synthetic Liquid Fuel Processes. Hydrogenation of Carbon Monoxide," Part I.

(7) Catalyst 108B; see ref. 6.

(8) The excess carbon can be accounted for as a monolayer of chemisorbed carbon monxide.

(9) Bahr and Jessen, *Ber.*, **63**, 2226 (1930); this laboratory, unpublished results.

results in the formation of not more than a monolayer of oxide or chemisorbed carbon monoxide[10]; since this is easily removed by hydrogen at 200° it might be expected to be removed by synthesis gas, and therefore to be not responsible for the inhibition. These experiments show, then, that bulk cobalt carbide is not a catalyst for the synthesis.

Bulk Carbide in Used Catalysts.—A second line of evidence which indicates that bulk cobalt carbide is not important in the synthesis is furnished by X-ray analysis of catalysts that have been used in the synthesis. It has previously been shown[11] that, on low-temperature carburization with carbon monoxide, reduced cobalt catalysts form a carbide, Co_2C, which has a characteristic X-ray diffraction pattern. This fact provides a means of identifying cobalt carbide in the catalyst. It has been observed by X-ray analysis that, if catalyst samples are partly carbided before synthesis and then used in synthesis, carbide is still present in the samples even after several days of synthesis. (In pure hydrogen, the carbide would have been completely removed as methane in several hours.) On the other hand, if the samples are used in the synthesis immediately after reduction (that is, no precarbiding), no carbide is found at the conclusion of the synthesis. In other words, bulk carbide apparently is not built up during steady-state synthesis in quantity sufficient to be detected by X-ray analysis, while carbide already present apparently is not removed at an appreciable rate during steady-state synthesis. Although quantitative determinations of the amount of carbide present under given conditions have yet to be made, the indication is that bulk carbide is neither formed nor destroyed as part of the synthesis process.

Cobalt in Used Catalysts.—The final evidence to be adduced in connection with the role of bulk carbide is also based on X-ray diffraction analysis. Cobalt in catalysts reduced at 400° is present primarily as face centered cubic cobalt.[11,12] There is a transition between face centered cubic cobalt and hexagonal close packed cobalt at about 400°.[13,14] The transition is very sluggish and there is an unusual type of disorder in the hexagonal structure near the transition point.[15] At the temperature of the Fischer–Tropsch synthesis on cobalt–thoria–kieselguhr catalysts (225° and below), the cubic cobalt is thermodynamically unstable with respect to the hexagonal close packed cobalt. Carbiding of the reduced sample containing cubic cobalt, followed by hydrogenation of the carbide so formed, both at 200°, always converts the cobalt to the low-temperature stable, hexagonal close packed form.[11] Now, all samples of cobalt catalysts (not precarbided) which have been examined after use in the synthesis have given a diffraction pattern identical with that of the freshly reduced catalyst. If any appreciable quantity of the cobalt had been through the cycle of carbiding and hydrogenation *at any time* during the synthesis, it would have appeared as close packed hexagonal cobalt rather than cubic.[16] Since this does not occur, it follows that, within the limits of the X-ray method, cobalt was not converted to bulk carbide and subsequently hydrogenated during the synthesis, that is, bulk carbide is not an intermediate in the synthesis.

Summary

Evidence is presented that for cobalt catalysts, bulk cobalt carbide is neither an intermediate in the Fischer–Tropsch synthesis nor a catalytically active substrate for the synthesis:

1. The presence of extensive amounts of carbide in cobalt catalysts severely inhibits the Fischer–Tropsch synthesis.
2. Used catalysts show no carbide by X-ray analysis, but samples carbided before synthesis show carbide to be present after synthesis.
3. The low-temperature unstable cubic cobalt produced by reduction of cobalt catalysts is not converted to hexagonal cobalt during the synthesis, although carbiding and subsequent hydrogenation of a reduced catalyst always results in this conversion.

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[10] This laboratory, unpublished results.

[11] Hofer and Peebles, THIS JOURNAL, **69**, 2497 (1947).

[12] The expected 200 line in the powder pattern of the reduced cobalt is almost entirely absent as has been previously mentioned.[11] A detailed discussion of this unusual diffraction pattern will be published. However, the unusual diffraction pattern of the cubic cobalt does not affect the validity of the reasoning concerning the function of bulk carbide in the Fischer–Tropsch reaction.

[13] Hendricks, Jefferson and Shultz, *Z. Krist*, **73**, 376 (1930).

[14] Emmett and Shultz, THIS JOURNAL, **51**, 3249 (1929).

[15] Edwards and Lipson, *J. Inst. Metals*, **69**, 177 (1943).

[16] Because of difficulties inherent in X-ray diffraction analysis this statement is not strictly correct. If, for example, the carbiding-hydrogenation cycle occurs only in the outermost 10–20 atomic layers of cobalt particles, this phase change may not be detected by X-rays. Also X-ray diffraction analysis under any conditions will not detect less than 5% of a minor crystalline constituent so that if less than 5% of cobalt went through this cycle, the change would not be detected.