

TRANSLATION OF OIL MISSION FILM REEL NO. 101,
Ft.3, Fr.10 to Ft.4, Fr.3
German Item No. 21559

Report on Research in the Field of Medium
Pressure Synthesis Over Iron Catalysts.
(Kaiser-Wilhelm-Institut für Kohlenfor-
schung Mülheim-Ruhr), dated June, 1940.

The Subject Matter on pp. 30-35 of the
Original, relating to "THEORY OF FORMATION
OF IRON CATALYSTS", has been translated.

4. Theory of Formation.

It was shown that for preparing an active iron catalyst it is necessary to have a preliminary treatment of the catalyst with carbon monoxide or gases containing carbon monoxide at temperatures of about 250 to 350°C. and that furthermore this process of "formation" must be carried out at lower pressure than the synthesis.

The reason why formation with carbon monoxide - hydrogen mixtures produces catalysts of somewhat lower activity than the one with carbon monoxide was stated to lie in that carbon monoxide and hydrogen react with each other during the formation, to give compounds which cause a fouling of the active surface of the catalyst to a varying degree.

A formation with hydrogen was not possible.

The radically different effect of the carbon monoxide and the hydrogen may be due firstly to the different reduction of the iron oxide, secondly to the loosening of the iron structure through the deposition of carbon formed during the carbon monoxide treatment, and thirdly to the formation of carbide during the action of carbon monoxide.

If diffusion, sintering, and carbon deposition be disregarded, then, as is known in literature, the reduction proceeds faster with hydrogen than with carbon monoxide. However, when working under conditions which take these points into consideration, the reduction with carbon monoxide may prove more favorable because of the loosening due to the intercalation of carbon (11).

The primary step of the reduction is the formation of ferromagnetic Fe_3O_4 . It was formed during the reduction with carbon monoxide as well as with hydrogen and may be obtained directly by precipitation from a mixture

of ferrous and ferric salts with alkalies and subsequent dehydration. It possesses however no catalytic properties with respect to medium-pressure synthesis.

In discussing the further action of the carbon monoxide, the equilibrium conditions of the iron - carbon - oxygen system should be pointed out. It depends upon the temperature, the gas pressure, and the ratio of carbon monoxide to carbon dioxide in the gas. Fig. 5a refers to atmospheric pressure. It contains data from the investigations by R. Schenck (12); the dot-dash curves were obtained by calculation by U. Hoffmann and E. Groll (15). Fig. 5b shows the equilibrium conditions at 1/10 atm. pressure. The Fe_2O_4 - Fe_3C curve was determined by taking into account the influence of pressure on the equilibrium values. The other curves were compiled on the basis of data given by Schenck in the above mentioned paper.

It may be seen from Fig. 5 that no FeO is stable at temperatures below 550 to 560°C. (FeO is termed "wüstite" by Schenck since it always contains Fe_2O_4). At lower temperatures the reduction of Fe_2O_4 proceeds without passing through the FeO phase.

The metallic phase is in stable equilibrium only at temperatures above 550 to 600°C. (this phase according to Schenck consists of oxoferrite containing oxygen and oxo-austenite containing oxygen and carbide). Thus, at lower temperatures the carbide is probably formed by direct action of carbon monoxide on Fe_2O_4 , or via unstable intermediate compounds containing less oxygen. U. Hoffmann and E. Groll, who investigated by X-ray analysis the deposits resulting from the passage of carbon monoxide over iron, always found only very small amounts of free iron, even at below 650°C.

Whereas the reduction of the higher iron oxides to the lower ones or to iron proceeds independent of pressure, e. i. depends only on the carbon dioxide - carbon monoxide ratio and on temperature, the conversions according to diagram 5b involving formation of carbide or carbon are shifted towards carbon monoxide by the use of lower pressure. An increase in pressure therefore favors formation of carbide and carbon. In the presence of a 100% carbon monoxide, as may be the case for instance with very fast flow of carbon monoxide over the catalyst bodies, only iron carbide is in equilibrium at 1 atm. as well as at 1/10 atm.

If an equilibrium should take place during the action of pure carbon monoxide on metallic iron, then carbide must be formed first, while the carbon dioxide formed simultaneously therewith has an oxidizing effect upon the iron. It appears reasonable that the formation of an iron catalyst, being a reduction process, will be favored by low pressures and high flow velocities of carbon monoxide since these factors decrease the partial pressure of carbon dioxide and make possible a rapid removal of the carbon dioxide adsorbed on the catalyst.

Cementite Fe_3C is the only carbide indicated in both diagrams and no higher carbide is included. Its existence was suggested for the first time in 1915 by Hilpert(14). F.Fischer and collaborators pointed out many times the formation of higher carbides as intermediate products in the gasoline synthesis. F.Fischer and H.Bahr(15) have also described such an iron carbide. Glund and collaborators(16) gave the formula Fe_2C to this iron carbide. U.Hoffmann and E.Groll in the above-mentioned paper, referring to products derived by the action of carbon monoxide on iron at temperatures below $400^{\circ}C.$, have proved the interferences of this carbide in their X-ray examinations and found that with increase in temperature over $400^{\circ}C.$ this carbide disappears at the expense of increased carbon formation. It is assumed that the decomposition takes place with formation of cementite and free carbon.

Little can be said as yet about the equilibrium conditions of the carbide or, perhaps, of the higher carbides. For this reason the existence region of this carbide could not be shown by curves or areas in Fig.5. It appears certain that low temperatures and high concentrations of carbon monoxide are necessary for its formation. These conditions correspond to the optimum formation conditions of the iron synthesis. Therefore it seems very likely that the presence of this compound in the catalyst is of decisive importance for the degree of formation and thus to the progress of the synthesis.

It goes without saying that this carbide must be formed not only prior to the synthesis by a suitable preliminary treatment but also, the lest synthesis should slacken within a short time, it must not undergo any decomposition during the synthesis or, if it occurs as an intermediate product, it must not break faster than it is reformed. A certain observation made during the synthesis points to the same conclusion. When the temperatures are too low (for example below $220^{\circ}C.$), the synthesis proceeds at a good conversion rate immediately after the formation. The rate however slows down gradually and cannot be increased again, even at higher temperatures (for example 230 to $240^{\circ}C.$) at which it would run if the reaction had been carried out at this temperature to begin with. (At lower temperatures it is likely that the carbide is being broken up by hydrogen faster than it could be reformed by the influence of carbon monoxide).

Furthermore it should be pointed out that the unusually high initial activity of the iron catalysts may be explained by the scheme of the diagram as well as by experiments which are still in progress at this date. After the formation, wherein an equilibrium has been established by using a high-percentage carbon monoxide, very little oxygen is present in the catalyst. In the synthesis however a gas is formed which contains 50 to 60% carbon dioxide and which must lead to a partial oxidation of the catalyst in conformance with the equilibrium conditions, the catalyst now showing a decreased activity. The fact that nevertheless the "best formed" catalysts

are always superior in the long run to the less extensively formed ones may be correlated also with structural changes in the catalyst occurring during formation.

As far as formation of free carbon is concerned, one may assume that it is speeded up catalytically by the carbide which is rich in carbon. To what extent this undesired decomposition of carbon monoxide in the presence of hydrogen may be prevented is the subject of investigations now being carried on. Certain is however that the formation of carbon, which occurs during formation, may be appreciably inhibited by lowering the pressure and increasing the flow velocity of the carbon monoxide.

Translated by:
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3/29/46