fact cannot be explained as resulting from limitation of the reaction to the surface of the catalyst particles, since it is known that variation of grain size between 1 and 5 millimeters does not affect the activity. When the grain size exceeds 5 millimeters, the catalyst distintegrates quickly because of insufficient heat removal. Because of its large internal surface, the catalyst is completely penetrated by the synthesis gas.

These results show that it is useful to distinguish between two groups of iron catalysts:

1. Copper-free iron catalysts pretreated with carbon monoxide at low pressure and 325°C. and operated at pressures between 10 and 20 atmospheres.
2. Iron catalysts with a high copper content pretreated with synthesis gas at atmospheric pressure and 225°C., which can be used both in atmospheric-pressure and in medium-pressure synthesis.

The results obtained with iron catalysts during medium- and atmospheric-pressure synthesis show that in the former, the carbide–oxide equilibrium is established during synthesis by a decrease in the amount of carbide that had been formed during pretreatment, whereas the latter reach equilibrium by gradually forming the carbide during treatment with synthesis gas at 220° to 230°C.

As a result of the low operating temperature and pressure, formation of free carbon was eliminated during operation at atmospheric pressure.

MECHANISM OF THE SYNTHESIS

These experimental results leave no doubt about the necessity of higher iron carbides in the Fischer-Tropsch process over iron catalysts. According to Fischer and Tropsch, these compounds act as intermediates that are continually hydrogenated and regenerated, the first reaction product being (CH_2) radicals. Craxford[16] thought he could explain the synthesis over cobalt in such a manner by showing that cobalt catalysts react with carbon monoxide at synthesis temperature to yield a carbide that can be hydrogenated at atmospheric pressure and 140°C.

The stability of iron carbides at synthesis temperature and the fact that metallic iron and cementite are not decomposition products in the synthesis make it seem likely that other products are important in addition to the carbides whose presence has been demonstrated thermomagnetically. These products are probably unstable and perhaps are surface combinations. When carburization and hydrogenation proceed simultaneously, (CH_2) radicals are formed and adsorbed as polymethylenes on the catalyst surface. With large amounts of chemisorbed hydrogen only methane is formed. If little hydrogen is present, predominantly straight-chain paraffins and olefins are desorbed, whose molecular size and degree of saturation are determined by the amount of chemisorbed hydrogen, by the contact time with the catalyst, and by the relative reducing and polymerizing activity of the catalyst.

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[16] Craxford, S. R. [Fischer-Tropsch Synthesis of Hydrocarbons and Some Related Reactions]: Brennstoff Chem., vol. 20, 1939, pp. 263–270.

DISCUSSION OF EXPERIMENTAL RESULTS AND SUMMARY

The composition of iron catalysts at various stages of pretreatment and synthesis in the Fischer-Tropsch process was determined by chemical and thermomagnetic analysis. During carburization of copper-free iron catalysts, free carbon was formed continuously, its rate of deposition increasing with longer contact time, higher pressure, and especially with higher carburization temperature. This formation of elementary carbon probably continued during medium-pressure synthesis, especially in the presence of carbon monoxide-rich gas and at high operating temperatures. The thermomagnetic method revealed that copper-free iron catalysts, carburized at 325°C. before medium-pressure synthesis, were virtually completely transformed to a ferromagnetic higher iron carbide with a Curie point of 265°C., whose formula corresponded approximately to Fe_2C.

Carburization of copper-promoted (20 percent Cu) iron catalysts at 220° to 230°C. before atmospheric-pressure synthesis yielded not only the 265°C. Curie-point carbide but also a second ferromagnetic iron carbide whose Curie point was 380°C. Thus higher iron carbides and their Curie points have been detected by the thermomagnetic method; they could not have been found by the hydrogen reduction method. At the same time, the theory advanced by Fischer and Tropsch concerning the formation of higher carbides in these catalysts has been confirmed experimentally. At 205°C. iron was carburized largely to the 380°C. Curie-point carbide. However, the 265°C. Curie-point carbide was always present. Consequently, the formula Fe_2C derived by Gluud and Ritter and by Bahr and Jessen for an iron carbide prepared at 220°C., does not correspond to a homogeneous compound.

A systematic study of the thermal stability of the higher iron carbides showed that the 265°C. Curie-point carbide is the more stable of the two. It reverts to Fe_3C above 400°C. without any marked change in the specific magnetization at room temperature. The 380°C. Curie-point carbide is unstable above 300°C. and is ultimately also converted to cementite above that temperature.

Determination, by acid decomposition, of the carbidic carbon content of carburized-iron catalysts always gave values that were only half those obtained by reduction with hydrogen at atmospheric pressure. This difference is explained by the formation of higher iron carbides whose decomposition by acid was not accompanied by quantitative hydrogenation of carbidic carbon, as in the case of cementite. Actually, almost half the carbon reverted to free carbon, which also explains the large amount of hydrogen evolved.

The higher iron carbides formed during carburization were stable during the synthesis. During carburization at 325°C. and during subsequent medium-pressure synthesis, the 265°C. Curie-point carbide was virtually the only carbide present. Carbide–oxide equilibrium was established during the first days of operation by partial oxidation of the large amounts of carbide that had been formed during pretreatment. Once equilibrium was established, active catalysts maintained their carbide content unchanged. A decrease in catalytic activity was marked by a drop in the carbide content and by an increase in the oxygen content. Thus, both acid decomposition and thermomagnetic analysis showed that the activity of iron catalysts in the Fischer-Tropsch process was higher when more carbide was formed during pretreatment.

Iron catalysts with a high copper content consisted of approximately equal amounts of 265°C. Curie-point and 380°C. Curie-point carbide during operation at atmospheric pressure. These carbided catalysts gave almost quantitative conversion of the carbon monoxide in water gas, with liquid and solid hydrocarbons as the principal products. When a catalyst thus carbided was operated at medium pressure (10 to 20 atmospheres) instead of atmospheric pressure, the optimum synthesis temperature dropped from 220°C. to 205°C. for the same conversion capacity. This increase in activity (compared with catalysts carburized at 325°C. with carbon monoxide) was probably due to the presence of the 380°C. Curie-point carbide, which characterizes atmospheric-pressure synthesis.

When the synthesis proceeded at a lower temperature, there was no formation of free carbon during carburization and synthesis; at the end of the pretreatment process carbide formation and conversion capacity had reached their maximum values, and no further carbon appeared. A current of hydrogen had little effect on the higher iron carbides in the temperature range of the synthesis.

In contrast to Hofmann's carburized pure iron, which always contained cementite, iron catalysts carbided up to 325°C. had no Curie point corresponding to cementite; but the thermomagnetic curves showed additional Curie points at 130° to 140°C. and at 425°C., probably due to potassium ferrite and copper ferrite, respectively.

These results make it necessary to modify Fischer and Tropsch's interpretation of the mechanism of hydrocarbon formation on iron catalysts. It now seems probable that the higher iron carbides do not themselves act as synthesis intermediates, but that they are important for the structure of the catalyst and that in their presence other products, such as surface compounds, may be formed.

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