

The Development of Fused-Iron Catalysts for the CO - H₂ Synthesis

(On the basis of researches by Dr. E. Linckh and Dr. R. Klemm)

In 1925 Dr. F. Winkler brought forward the suggestion of making gaseous olefins from coal or water gas. To this end Dr. Eduard Linckh had begun to conduct experiments in 1926 for the purpose of producing gaseous hydrocarbons with catalysts, in particular ethylene from water gas.

At this time there already existed long-established BASF patents dealing with the preparation of liquid hydrocarbons along with oxygen-containing compounds with the aid of catalysts under high pressure. Orlov was supposed to have obtained gaseous olefins with nickel catalysts. The initiated experiments were conducted with this report in mind, but the information could not be verified. However, Dr. Linckh soon succeeded in producing noticeable quantities of gaseous olefins under ordinary pressure and at 100° C. with copper catalysts for the first time. An increased yield, however, could not be achieved. The experiments were therefore extended to include iron catalysts. Substantial quantities of gaseous olefins were thereby obtained under high pressure. Final gases containing 13 per cent by volume of olefins were supposed to have been obtained. Later, however, interest reverted to the recovery of liquid hydrocarbons. As a result of these researches Dr. Linckh succeeded in developing serviceable fused-iron catalysts for the synthesis. The technique of preparing these catalysts depends almost entirely on the production of the conventional ammonia synthesis catalysts. Carbonyl iron powder was always employed as the starting material for the preparation of catalysts.

It is intimately mixed with added substances having a promoting action and melted in water-cooled crucibles with a blast of oxygen. The resulting molten lumps contain the iron in the form of oxides, principally as Fe_3O_4 . The molten cakes are broken up into suitable particle sizes.

They are treated with hydrogen to prepare them for the synthesis. This reaction takes place at temperatures ranging from 450 to 650 degrees. The reduction temperature, however, can be still further lessened by the use of high pressure.

In this manner Dr. Linckh investigated more than 1000 assorted catalysts. Unfortunately, the detailed results of these researches were lost as a result of the war and of the death of Dr. Linckh toward the end of the war.

The catalysts covered by German patent 708512, November 14, 1935, French patent 812290, English patent 465668 have remained of lasting value for us. The catalyst identified by Expt. No. 997 became the standard catalyst for all our later technical development researches.

This catalyst is produced by admixing

25 grams of silicon powder
25 grams of titanium oxide
50 grams of potassium permanganate
50 grams of water

to 1 kilogram of iron powder. In place of potassium permanganate the equivalent amount of manganous oxide, pyrolusite (MnO_2), or manganese powder and potassium hydroxide can be used without impairing the effectiveness of the catalyst. If these catalysts are treated at 650 degrees, the reaction will proceed rapidly and, on completion of reduction and cooling, will be rather insensitive to air. However, these catalysts are only

sufficiently reactive for the synthesis at pressures of 100 atm. gage and over. On the other hand, if the reaction is conducted at temperatures ranging from 450 to 500 degrees, the catalysts will develop a reactivity favorable for synthesis at medium pressures ranging from 15 to 25 atm. gage. However, since the catalysts are markedly pyrophoric, special precautionary measures must be applied in this instance to prevent the catalyst from burning in air. Transference in the synthesis reactors therefore takes place with exclusion of air in the presence of carbon dioxide, or in case of synthesis, in a liquid medium by soaking or dipping in oil. Reduction at low temperatures possesses the additional disadvantage of a duration of 5 - 6 days. The hydrogen is recirculated above the catalysts and is dried before admittance into the reaction vessels. This drying is advantageously accomplished in a silica gel drying installation.

Dr. Linckh endeavored to develop the iron catalysts to a point where the synthesis could be conducted at ordinary pressure with a good yield. He believed that this was achieved by the addition of antimony or arsenic to the iron catalysts. However, as a result of the war, practical tests on these catalysts were no longer carried out.

Linckh made the interesting proposal that etched metal disks and the like be employed instead of catalysts (German patent 721359, French patent 805696, English patent 458035).

The fused iron catalysts were developed further by Dr. Richard Klemm, to be used for a specific purpose, viz., to attain the greatest possible yields of ethyl alcohol.

It is no longer necessary to abstract these researches at this point because a relevant original report can be appended (see report of Dr. Klemm, July 1, 1944).