

I. The Catalysts

A. Precipitation of Catalysts.

We have started at first with the view point, that

variations in the method of preparation of iron catalysts or certain additions to them, could affect the course of reaction of synthesis at atmospheric pressure by increasing the yield of liquid hydrocarbons. Many hundreds of different iron catalysts have been prepared with a greatest variety of additions and by different methods of precipitation.

It has, however, been found in the course of our work that the required objectives could only be reached when operating under a slight pressure, but in that case the iron catalysts used could be prepared in a great variety of ways. If catalysts were subjected to a certain pretreatment (forming) before being put in operation with gases containing carbon monoxide under pressure, catalysts consisting of iron alone could be used for many months to synthesize a satisfactory yield of the required hydrocarbons from carbon monoxide and hydrogen.

1. Raw Material

Solutions of iron salts were generally used as raw material for the preparation of iron catalysts, and these solutions were prepared by dissolving a technical grade of iron. For comparison tests were made with the commercial C.P. grade of iron salts. Most of the tests were made with the following iron compounds.

- a. Ferric nitrate (C.P.)
- b. A solution of mostly tri-valent iron nitrate prepared from technical iron filings. For its preparation small proportions of iron filings were added to nitric acid of an original Sp. gr. of 1.18, without permitting the temperature to exceed 40 - 50°C (above 60 - 70°C the nitrate decomposes with the formation of insoluble compounds).
- c. The ferrous nitrate solution was prepared by using a nitric acid of a maximum Sp. gr. of 1.05 and iron filings, maintaining the temperature at 35 - 40°C. (Higher acid concentration or higher temperatures resulted in conversion of the ferrous into the ferric form, in a violent reaction).
- d. Ferrous chloride

2. Precipitation with Sodium Carbonate

The concentration of the iron solution used for precipitation was in general 1 kg of iron in 30 li of solution (for divalent and trivalent catalysts). The solution was first neutralized in the cold with a concentrated solution of sodium carbonate, until the precipitate just redissolve. The ferric solutions were precipitated mostly at 100°C, the ferrous solutions at a maximum temperature of 70 - 75°C, using slight excess of sodium carbonate. As a rule the solutions contained 1 kg of soda to 8 - 10 li of water. After precipitation, the solution was briefly heated to boiling, filtered and washed with hot distilled water until free from alkali. The moist precipitate was again suspended in distilled water, mixed on a water bath until homogeneous, and with the required amount of alkali (in most cases potassium carbonate dissolved in water) with a steady stirring. Most of the water was evaporated on the water bath with continuous stirring. The catalysts was next heated overnight in a drying oven at 110°C, granulated and freed from dust. The "ferric catalysts" are black-brown, rather hard, and have mostly a vitreous fracture. The ferrous catalysts are voluminous and earth-brown.

The ferric catalysts precipitated with sodium carbonate have been found in general to be superior to the ferrous catalysts. For this reason catalysts made from the ferric nitrate solutions of technical grade of iron were used in most tests and designated as the normal iron catalysts.

Two points in particular must be borne in mind during their preparation: 1. the preliminary neutralization of the iron solution must be done in the cold, since otherwise when heating, or even after long standing, turbidity would form in the solution because of deposition of insoluble salts, and this would affect the reproducibility of a good catalysts. 2. The boiling of the iron precipitate before filtration was important for the activity and the life of the catalysts. This can be seen in table 1. There catalysts prepared under different temperature conditions are compared with each other. The contraction during synthesis (carbon monoxide - hydrogen mixture 3 : 2, 15 atm., 235°C), was used as a measure of the activity after differently long use.

long use.

The greatest possible contraction with an assumption of a 100 percent conversion to liquid hydrocarbons according to the equation $2\text{CO} + \text{H}_2 = \text{CO}_2 + \text{CH}_2$ is 60 percent with a synthesis gas contains 10 percent of inert constituents. Actual contractions of 50 - 55 percent were observed in the best yields.

Table 1.

Effect of Temperature of Precipitation upon the Activity of Iron Catalysts

Precipitation Temp. °C	Heated to boiling after Precipitation	Alkali Content	Days of Operation				
			1	2	5	10	20
20	No	1	43	-	44	43	-
60	"	1	50	-	33	20	-
20	Short	1	50	-	48	51	-
20	"	1/4	-	50	48	51	50
20	1 minute	1/4	55	55	48	48	50
20	5 "	1/4	-	56	-	47	48
100	1 "	1/4	50	50	50	49	56

This table shows that the two catalysts not heated to boiling either failed to develop full activity or else lost it very rapidly. Catalysts heated briefly to boiling and those boiled for one minute were equally good. Longer heating brought no advantages. The last test where precipitation was done at the boiling point represents the normal iron catalysts.

3. Precipitation with Ammonia

A stream of ammonia was lead into solution of ferric nitrate at 60°C containing 100g of iron/li. The rate of flow of the gaseous ammonia was in general so regulated that the precipitation was complete in twenty minutes. Until the end of the precipitation, ammonia is quantitative absorbed. An equal volume of boiling distilled water was added to the pasty precipitate, the mixture filtered and the precipitate washed five times with hot distilled water. The subsequent alkalization was done in the same way as with the catalysts precipitated with sodium carbonate. The iron catalysts precipitate with ammonia are black-brown, hard and have a vitreous fraction.

4. Addition of Kieselguhr

Iron-kieselguhr catalysts have been used in a number of tests. They will be discussed in a special section. In general the addition of kieselguhr was done after the alkalization, during the evaporation of the catalyst mass on the water bath. The previous dispersion of the kieselguhr in distilled water offers an advantage. It will prevent a too rapid elimination of water from the catalyst mass and the formation of non-homogeneous lumps.