

## CHAPTER IX.I

### SUMMARY

During the course of the three years of work to accomplish the targeted objectives, eight 1-liter continuous stirred autoclave reactors were acquired and installed together with the needed equipment to clean the synthesis gas, to obtain accurate gas flows over 2- to 4-month periods, and to collect the reaction products. Analytical equipment was installed that utilized two on-line gas chromatographs to permit a detailed analysis of the gaseous products of the noncondensable unconverted reactants and products as well as hydrocarbons up to C<sub>9</sub>. Liquid products up to about C<sub>30</sub> were analyzed on a routine basis. Mass balance samples were collected twice a week.

During the contract more than 100 runs were made to evaluate the activity and selectivity of catalysts prepared at the CAER and at United Catalyst, Inc. for testing at LaPorte, Texas. These runs, when the catalyst exhibited sufficient activity, continued for up to 4 months.

For the low alpha catalyst, both the targeted CO conversion activity and the maintenance of activity were met and exceeded. The activity testing showed that catalysts with reproducible activity and selectivity could be prepared using a continuous precipitation process. The catalyst preparation was carried out at a scale exceeding the targeted productivity (100 pounds/week) for the catalyst preparation process and it was shown that both the selectivity and activity of the large batch preparation duplicated that of the smaller catalyst preparations carried out at the laboratory scale.

The catalyst testing identified the optimum level of alkali promoter as 0.5 wt.% for both silica and alumina containing iron catalysts. With the alumina containing iron catalyst, it appears that the optimum aluminum level is about 6 wt.%. For the silica containing catalyst it does not appear that the content of silica in the range of 0 to 10 wt.% has an impact upon the activity. It was demonstrated that the alkali does not have an impact upon the initial CO conversion for early periods of the reaction (up to about 300 hours) but that it does have a great impact upon the rate that a catalyst declines in activity. Again, a catalyst with about 0.5 wt.% K appears to have the superior activity maintenance.

Kinetic measurements indicate that the rate of hydrocarbon synthesis decreases with CO conversion levels. For higher CO conversion levels, CO and H<sub>2</sub> conversion rates become about equal. Likewise, the selectivity causes hydrogen conversion to exceed that of carbon monoxide at lower CO conversion levels but that the conversions of carbon monoxide exceeds that of hydrogen at higher CO conversion levels. It was shown that the dependence of reaction rate on the CO conversion levels would allow operation with recycle to effect conversion at about 66% CO level at a syngas feed rate of about 6.6 NL/hr.-g(Fe) rather than the 3.1 NL/hr.-g(Fe) that would be possible if the process was operated to effect 90% CO conversion in a single pass reactor.

The structural promoter - silica, alumina or zirconia were used in this study - can be added during the precipitation step or following precipitation and drying using an impregnation procedure. The most economical form of silica is water-glass. However, adding water-glass to the acidic iron(II) or iron(III) solution leads to the precipitation of large particles of silica, and this produces a very poor distribution of the silica in the final catalyst formulation. In the present study, silicon tetrapropoxide was hydrolyzed in a neutral or slightly basic solution to provide a colloidal or smaller particle size dispersion of silica. Adding this freshly formed silica to the acidic iron solution produced a clear solution after standing overnight. Thus, the preferred procedure for the incorporation of silica during the precipitation step is to utilize silicon tetraalkyloxide. In addition, the preferred procedure does not add alkali as is the case when water-glass is utilized.

The material prepared by precipitation from an iron(III) nitrate solution with ammonium hydroxide remains amorphous to X-ray diffraction even following calcination at 300°C for 24 hours. This clearly shows that very small particles of iron oxyhydroxide or oxide are formed by this procedure.

Methods have been utilized to produce  $\alpha$ -,  $\gamma$ - or  $\delta$ -FeOOH by the oxidation of iron(II) sulfate solutions. The maximum surface areas that have been obtained for variations of the procedures used to produce these materials fall in the 50 to 150 m<sup>2</sup>/g range, and usually the area of the material is at the lower end of this range. Oxidations have been effected by air, oxygen and hydrogen peroxide. For all three oxidants and starting at a pH of about 8, the oxidation rate is controlled by diffusion of the oxidant. The oxidation is significantly exothermic so that precipitation

temperatures below about 35-40°C can be utilized only by providing a means of cooling the reactor or using a very slow rate of addition of the reactants.

When the precipitation is effected from an iron(II) sulfate solution it has been found that it is difficult to remove the sulfate by washing. The amount of sulfate removed with each washing appears to approximate an exponential decline; thus, it is a very demanding task to wash the precipitate a sufficient number of times to even reduce the residual sulfate level in the solid to about 0.5 wt.%. Since sulfur, at least in the reduced form of  $H_2S$ , is a severe catalyst poison, there is risk involved in using the sulfate salt as the source of iron.

The alkali promoter could, in principle, be added during the precipitation or by equilibration of the precipitate in a solution containing a salt of the desired alkali promoter. However, the adsorption (ion exchange) isotherms show a nearly linear relation between the amount of alkali ion adsorbed and the concentration of the alkali ion remaining in solution. This means that much of the alkali metal ion will be removed during each washing step unless the wash contains a significant amount of the ion. Likewise, adding the metal ion by equilibration will make it difficult to control the total amount of alkali in the finished catalyst because any occluded aqueous solution will contain the alkali metal ion. For these reasons, it appears that a preferred procedure is to add the alkali metal ion by an impregnation technique that does not involve an equilibration. The incipient wetness approach, where an amount of the aqueous metal ion solution is added that will nearly wet the powder, is preferred since the total amount of alkali in the finished catalyst can be easily controlled. Another approach is to utilize an organometallic compound, such as potassium t-butoxide, and

either an aqueous or organic solvent. The organometallic salt may be added by the incipient wetness impregnation technique or the alkali metal salt may be added to the reactor containing the catalyst to be impregnated as a suspension in the start-up solvent. The addition of the alkali metal to the suspension in the reactor has an advantage since additional alkali can be added during the course of the reaction.

Copper can be added by impregnation using an aqueous copper nitrate solution, preferably using the incipient wetness technique. Most preparative procedures which involve a precipitation step utilize sodium carbonate to adjust the pH, usually in the 5-7 range, if copper is to be added during the precipitation step. However, some work indicates that up to 1 wt.% copper can be incorporated by ion exchange during the precipitation procedure even when ammonium hydroxide is used to adjust the pH.

A large batch (about 150 lb.) of catalyst has been prepared by a continuous precipitation process followed by two washings and then spray drying. The finished catalyst had activity and aging characteristics that approached closely the target values.