

VI. SUMMARY

The activation and characterization of a number of catalyst formulations have been accomplished during this study. The results indicate that a pretreatment for 24 hours with CO at the conditions to be utilized for the synthesis is likely to provide a finished material with a high activity for synthesis. It is possible to activate an iron based catalyst with a synthesis gas mixture but it appears that each catalyst formulation will require a specific recipe and, in general, the first effort may not yield a material with the maximum activity attainable for the particular catalyst formulation.

A series of pretreatments were conducted in which carbon retention was followed by monitoring the level of CO₂ in the exit gas during various stages of the 24 hour pretreatment step. There is an initial, rapid reduction of the catalyst to produce nearly pure Fe₃O₄; this is generally accomplished during the 2-4 hour heat-up period. There is then a decline in the rate of CO₂ production and this is followed by a slow increase in CO₂ production. After 7-10 hours a maximum in the rate of CO₂ production is reached after which the production rate declines to asymptotically approach zero. However, even after 24 hours of activation in CO, and the deposition of two times as much carbon as is needed for the reaction to produce Fe_{2.2}C, carbon continues to deposit. Interrupting the activation when the carbon deposition is equivalent to the stoichiometric reaction to produce Fe_{2.2}C leads to a material that has only about half, or even less than half, the activity of a material that has been pretreated for 24 hours. Likewise, interrupting the activation following the reduction to produce nearly pure Fe₃O₄ leads to a material that is nearly inactive for the conversion of synthesis gas.

It has been demonstrated by X-ray diffraction and by Mössbauer spectroscopy that the material following 24 hours in CO is essentially an iron carbide. However, chemical analysis of the material activated for 24 hours clearly shows an excess of carbon over that needed to produce iron carbide; thus, some form of carbon that is amorphous to X-rays is present. During synthesis at 270°C and 7 atm. with a H₂/CO = 0.7 mixture, there is a gradual conversion of the carbide to Fe₃O₄. During this conversion, the activity and selectivity (product distribution as defined by alpha and product selectivity as defined by olefin/paraffin distribution) remain essentially constant. This observation is true for iron carbides prepared from the reaction of a precipitated iron with CO or from an iron carbide obtained from a laser pyrolysis technique using iron carbonyl and ethylene as reactants. The conclusion is not as clear as to the relative activities of the particular types of iron carbide; that is, it remains to be defined whether the various carbide phases lead to the same catalyst after a few hundred hours on-stream. The data point to some form of iron-carbon structure as being responsible for the catalytic site that is active for the synthesis; presumably this iron-carbon structure is supported on the bulk Fe₃O₄ that is observed to be present in any of the active catalyst formulations after a few hundred hours of use.

For catalyst formulations that are not very active, e.g., those where CO conversion levels of 20% or less are obtained, the carbide phase will be retained in nearly all cases. Thus, an examination of the catalyst to determine the phase present at the end of the run does not necessarily provide a reliable measure of the catalyst during the period of high activity.

The data in this chapter make it clear that pretreatment in CO for 24 hours leads to an active material if, indeed, the catalyst formulation has high activity. The data also clearly show that the bulk phase may change from that of essentially an iron carbide to that of essentially Fe_3O_4 without a corresponding change in either the catalytic activity or selectivity. This observation points generally to both catalytic activity and selectivity being controlled by the structure of the surface layer(s), and not the bulk structure.

The studies show that the catalyst particles formed by spray drying do not survive 24 hours of agitation in an autoclave; this is true for the oxide or carbide form of the catalyst and does not depend upon whether the pressure is provided by an inert gas or the synthesis gas. The data clearly show that the spherical particles formed during spray drying and calcination survive 24 hours of pretreatment in CO provided this operation is carried out in a slurry reactor with agitation provided by gas flow. The carbided material does attrite during a modified ASTM attrition test; thus, rolling for about 500 hours reduces the average diameter of the spheres to about half the original value. Examination of the material following various periods of attrition indicate that the attrition is due to a slow erosion of material from the surface and not due to fracture of a spherical particle into many smaller particles. The carbided material, present in about 60 micron spheres, is reduced almost completely to the 1-2 micron particles making up the larger spherical particle during operation in the CSTR.

During the 24 hour pretreatment the surface area for the precipitated iron catalyst undergoes a rapid decline from about $300 \text{ m}^2/\text{g}$ to about $60 \text{ m}^2/\text{g}$. During a subsequent period of synthesis of up to 2,000 hours, there is a gradual decline in

surface area; however, it appears that at least a significant fraction, if not all, of this decline is due to the inability to extract all of the wax deposited, and this increases with time on stream. The loss in surface area appears to be less for a pretreatment in CO than in either a syngas mixture or a pretreatment consisting of first reducing in hydrogen and then exposure to a synthesis gas.