

IV. SUMMARY

The preparation of precipitated iron catalysts has been accomplished starting with aqueous solutions of either Fe^{2+} and Fe^{3+} . Medium to high surface area catalysts can be prepared from salt solutions containing iron in either oxidation state. As shown below, it appears that it is preferable to utilize Fe^{3+} , and specifically the iron(III) nitrate salt;

Iron(II) sulfate solutions are readily available and are an economical source of iron salt. A major reason for this is that sulfuric acid is utilized to remove rust from the finished products from steel-making. The oxidation rate of iron(II) is very slow in solutions as are acidic as utilized by the steel manufacturers, and this is the reason for the production of iron(II) solutions.

As shown in Figure IV.3.15 the half-life for iron(II) oxidation decreases logarithmically with the pH. Thus, the half-life for iron(II) in a solution with a pH of 13 is extrapolated to be less than one second. This means that any oxidation at this pH will be controlled by the diffusion of the reactants.

The moderately rapid precipitation (6 minutes in the reactor) of hydrous iron oxyhydroxide or oxide from an iron(III) nitrate solution by the addition of concentrated ammonium hydroxide produces a very high surface area material (about $300 \text{ m}^2/\text{g}$). This surface area indicates that the spherical particles that are formed by precipitation have a diameter of about 3.0 nm and are essentially nonporous. Ultrafine iron oxide can be prepared by the flame oxidation of iron carbonyl to produce a material with a surface area of about $300 \text{ m}^2/\text{g}$. The ultrafine iron oxide obtained from the iron carbonyl is expensive; laboratory quantities cost more than \$100/lb. The individual

particles obtained from iron carbonyl and by the CAER precipitation process have essentially the same size and surface area. However, it is much cheaper to produce the material by the precipitation procedure. Drying of the precipitated material leads to agglomeration of the 3.0 nm particles because of the hydrostatic forces developed at the contact points of the small particles. With alumina, it has been possible to eliminate the agglomeration by washing with absolute alcohol to remove most of the water and then evaporating the alcohol above the critical temperature and pressure. Presumably this procedure could be utilized for the precipitated iron material; however, it is very difficult to carry out the supercritical solvent evaporation using a continuous process.

Ammonium hydroxide was utilized in the present study. There are at least two major advantages for using this base to effect the precipitation. When the precipitation is effected in the range of 9 to 10, the buffering action of the salt of the weak base makes it very easy to control the pH. Thus, even sudden changes in the flow rates of the reactant streams do not significantly alter the pH in the precipitation reactor; however, a strong base such as sodium hydroxide does not provide such buffering action. Secondly, ammonium nitrate or ammonium sulfate is formed during the precipitation process. Ammonium nitrate decomposes below 200°C so that the salt does not have to be completely removed by washing, and this decreases the total number of washings needed to be incorporated into the catalyst preparation procedure. When an alkali salt, e.g., NaOH or Na₂CO₃, is used the alkali metal must be almost completely removed during the washing step since its incorporation makes it difficult to provide the proper level of the alkali promoter in the finished catalyst.

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 α -, γ - or δ -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 m²/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