The Fischer-Tropsch Synthesis and Methanation

R. B. Anderson
McMaster University

Reactors for these processes involve difficult engineering problems, particularly concerned with removal of the heat of reaction; however, these tasks seem within the scope of expertise and experience of chemical engineering in the United States. The most urgent problems involve the durability and selectivity of catalysts. Of immediate concern are iron catalysts for the Fischer-Tropsch synthesis that will withstand disintegration by elemental carbon deposition and oxidation, and for nickel methanation catalysts resistance to disintegration by elemental carbon deposition and deactivation by carbide formation.

Longer range studies on a small scale, about 10 cc of catalyst, should examine metal catalysts including the iron-group metals and ruthenium, and other metals that are not normally effective in hydrogenation of oxides of carbon. Here, highly dispersed metals in the form of alloys and interstitial compounds such as carbides, nitrides, and borides should be tested. In addition to improved activity, selectivity, and durability, catalysts with moderate tolerance to sulfur compounds should be sought, i.e., catalysts that can be used successfully with 10 ppm of sulfur compounds, typical of the gas from efficient CO_2-scrubbers, such as the hot carbonate process.

Consideration should also be given to the methanol and isobutanol syntheses. The products of these processes can be used without elaborate separation and refining steps, and the alcohols are excellent motor fuels.

A. Sulfur-tolerant catalysts. Since sulfur must be removed somewhere in the process, catalysts that will operate on raw synthesis gas may be of little economic value. The upper limit suggested by Fischer in 1935, 1 to 2 mg S/m^3 (0.7 - 1.4 ppm), still seems valid for conventional catalysts. Increasing this limit to 5 - 10 ppm would bring the sulfur content within the capability of the hot carbonate and other CO_2-scrubbing processes for H_2S and COS. Removal of organic sulfur to this level would require other treatment, such as charcoal or iron oxide.

B. Fischer-Tropsch processes may be usefully considered in two classes:

   1. Those in which the catalyst is "soaking wet" with waxes and oils, both liquid at synthesis temperature; e.g., iron catalysts at 7 - 30 atm. and temperatures less than 275°C and cobalt catalysts at less than 210°C and 5 - 20 atm.
   2. Catalysts that are essentially "dry;" e.g., iron catalysts at > 325°C, and methanation catalysts.
   3. For iron catalysts, the synthesis gas is initially a reducing and carbiding reagent, but as the H_2 and CO

are consumed, H_2O and CO_2 become large enough to oxidize metallic iron and carbides. This effect is enhanced by diffusion-in-pores problems. Oxidation during synthesis apparently eliminates metals such as chromium.

D. For iron, the metal, the several carbides, nitrides, and carbonitrides are active catalysts. For cobalt and nickel, the metal is active but carbides are not. Oxides may be regarded as inactive, with Fe_3O_4 as a possible exception. Ruthenium metal is highly active; the carbide has not been tried to my knowledge. Platinum group metals are essentially inactive in the hydrogenation of CO and CO_2, probably due to CO being adsorbed very strongly upon them. Mo and W seem to meet criteria of not being too easily oxidized, but no useful catalysts have been reported.

E. Generally, the rate increases with increasing operating pressure at a given temperature until the formation of metal carbonyls begins. The best operating pressure is usually significantly lower than that required for carbonyl formation.

F. Alcohols are good fuels for motor vehicles and the methanol and isobutanol syntheses should not be ignored. Here, virtually all separation and refining steps are eliminated. Furthermore, nitrided iron catalysts provide large yields of ethanol plus some higher alcohols, and have better stability than other iron catalysts at temperatures below 270°C.

G. The hydrogenation of carbon oxides in processes usually considered are relatively slow reactions on the basis of weight of useful product per unit volume or weight of catalyst. For example, these processes seldom operate at hourly space velocities exceeding 1000 compared with space velocities in the ammonia synthesis of 20,000 or higher.

H. Iron catalysts for the Fischer-Tropsch synthesis have been studied extensively by physical chemists at the Bureau of Mines and elsewhere by relatively modern methods. Nickel catalysts for methanation have not been studied in detail. The current work of the Bureau of Mines on sprayed Raney nickel is a remarkable development involving a fortunate intuitive engineering attack without appreciable scientific support. In many respects, Raney nickel is different from other nickel catalysts and it should be studied in detail in the context of the tube-wall reactor to investigate carbide and elemental carbon formation. It should be noted that most of these problems would be avoided by hydrogenating CO_2 rather than CO.