4.4 CONCLUSIONS

4.4.1 General

- A mathematical mechanism has been developed which, when incorporated into models of three completely different reactor systems operating at completely different operating conditions with Fischer-Tropsch catalysts of different manufacture, gives reasonably good agreement on correlating rate constants derived from the experimental data published for these systems.

- The mechanism, as demonstrated for potassium-promoted catalyst, allows interpretation of yield differences resulting from different catalyst formulations.

- As demonstrated for the tube-wall reactor study of the Parsons design, the reactor models can be used to evaluate existing conceptual designs not only in terms of gross product yield but also in terms of reactor design and operating conditions.

- Because of the success of this mechanism in describing inherent strengths and weaknesses in a variety of Fischer-Tropsch reactor systems, work is proceeding on eliminating some of the mechanism deficiencies, thereby providing additional support to conclusions already drawn and providing additional insight into product yields.

- The largest influence on product yield is the relative concentration of H_2 and CO. The latter concentration is of particular importance when the order of reaction with respect to each component is assumed to be unity, since hydrogen's influence on the competition between the rate of polymerization and the rates of termination is minimal under these circumstances.

- Of all operating parameters (excluding catalyst), temperature has the strongest influence on gross product yields. An increase in reactor temperature results in an increase in CO conversion and a decrease in degree of polymerization.

- An increase in pressure results in an increase in CO conversion. If pressure is increased and the CO conversion is maintained constant by a corresponding increase in space velocity, the degree of polymerization will increase.

4.4.2 Tube-Wall Reactor

- The plug flow nature of the tube-wall reactor results in significant changes in the concentration of CO as a function of reactor length. This concentration profile has a marked effect on the degree of polymerization at any point in the reactor.

4.4.3 Entrained Bed Reactor

- As in the case of the tube-wall reactor, the entrained bed reactor is plug flow and, therefore, has a varying degree of polymerization as a function of reactor length. However, because of the large gas recycle rate, the conversion per pass is lower resulting in changes which are less dramatic.

- The high CO_2 concentration in the recycle gas results in a water-gas shift reaction which is near equilibrium throughout the entrained bed reactor.

- In the entrained bed reactor, catalyst circulation rate can be used as an operating parameter to adjust catalyst density within the reactor. Increased catalyst density increases CO conversion without significantly influencing the gross product yields.

4.4.4 Slurry Reactor

- Unlike the tube-wall and entrained bed reactors, the slurry reactor is back-mixed, and the CO and H_2 concentrations are uniform throughout the reactor. Consequently, the degree of polymerization is uniform and is set by CO and H_2 conversion.

- The water-gas shift is far from equilibrium in the slurry reactor and supplies a significant portion of the hydrogen required for conversion to hydrocarbon.

- The influence of mass transfer on the CO conversion and degree of polymerization at the operating conditions of Koelbel's slurry reactor is small.

4.4.5 Reactor Comparisons

- At the operating conditions proposed in the literature for these systems, the slurry reactor will inherently have a higher thermal efficiency than the entrained bed or tube-wall reactors because of the more efficient use of the water-gas shift reaction.

- The sensitivity of slurry reactor product yields to changes in temperature and CO conversion is superior to that in the entrained bed and tube-wall reactors.

- The entrained bed reactor lacks the operating flexibility of the tube-wall and slurry reactor systems.

4.5 MECHANISM IMPROVEMENTS

The mechanism as presented in Section 4.1 reasonably describes the gross product yields for three different reactor systems, and is adequate for comparing inherent strengths and weaknesses of these systems. The success of this approach, coupled with a desire to improve Fischer-Tropsch technology through its application to other reactor systems, has created a

need for expansion of the existing mechanism. A schematic of the proposed expansion is presented in Figure 4.5-1 with the original mechanism shown as black lines.

4.5.1 Free Carbon and Methane

Two undesirable components which require special treatment are free carbon and methane. Catalyst deactivation as well as reactor operational problems have been attributed to the formation of free carbon. In addition, methane is typically found in quantities significantly higher than predicted by simple Schulz-Flory kinetics and, therefore, lowers the production of gasoline and other more desirable products. Dry (6) has proposed a mechanism that not only accounts for the production of free carbon but also suggests a method for methane formation parallel to the hydrogenation of the active intermediate, $M(CH_2)_nH$, described in the original mechanism. Activated carbon and oxygen species are formed by the dissociation of an absorbed CO molecule. The activated oxygen can react with either H_2 or CO to form H_2O and CO_2, respectively. The activated carbon can either react with H_2 to form methane or it can form free carbon. These improvements can be incorporated into the original mechanism as indicated in red in Figure 4.5-1.

4.5.2 Alcohols

Oxygenates, primarily in the form of alcohols, frequently make up a measurable portion of the Fischer-Tropsch product. Normally these are undesirable products, and in the case of nitrided catalysts, which generally are more stable than standard F-T catalysts, they can make up more than 8 wt-% of the total product (58). In addition, F-T alcohols as feed to the Mobil's ZSM-5 catalyst have been shown to give a very selective product. For these reasons, consideration has been given to the incorporation of alcohols into the original mechanism shown in blue in Figure 4.5-1. The similarity of the mechanisms for the production of alcohols and olefins is apparent and is based on the work of Pichler and Schulz (37). Evidence suggests that alcohols, just as olefins, can initiate chains by readsorption on the catalyst sites, thus creating an equilibrium adsorption-desorption between product and catalyst.

4.5.3 Aromatics via Zeolites

The most significant problem in converting synthesis gas to gasoline using standard Fischer-Tropsch catalysts has been the lack of hydrocarbon selectivity. Recently, Mobil discovered a way to circumvent this problem by introducing the concept of a "shape selective" zeolite catalyst. Early approaches combined the Fischer-Tropsch and zeolite functions into a single "bifunctional" catalyst. This approach improves the normal F-T yield structure, away from a typical Schulz-Flory type distribution, by increasing total aromatic yield, reducing olefinic and paraffinic hydrocarbons and decreasing the average carbon number of the product. In addition, compounds above carbon number 11 were significantly reduced to less than 3 wt-% of the total yield.

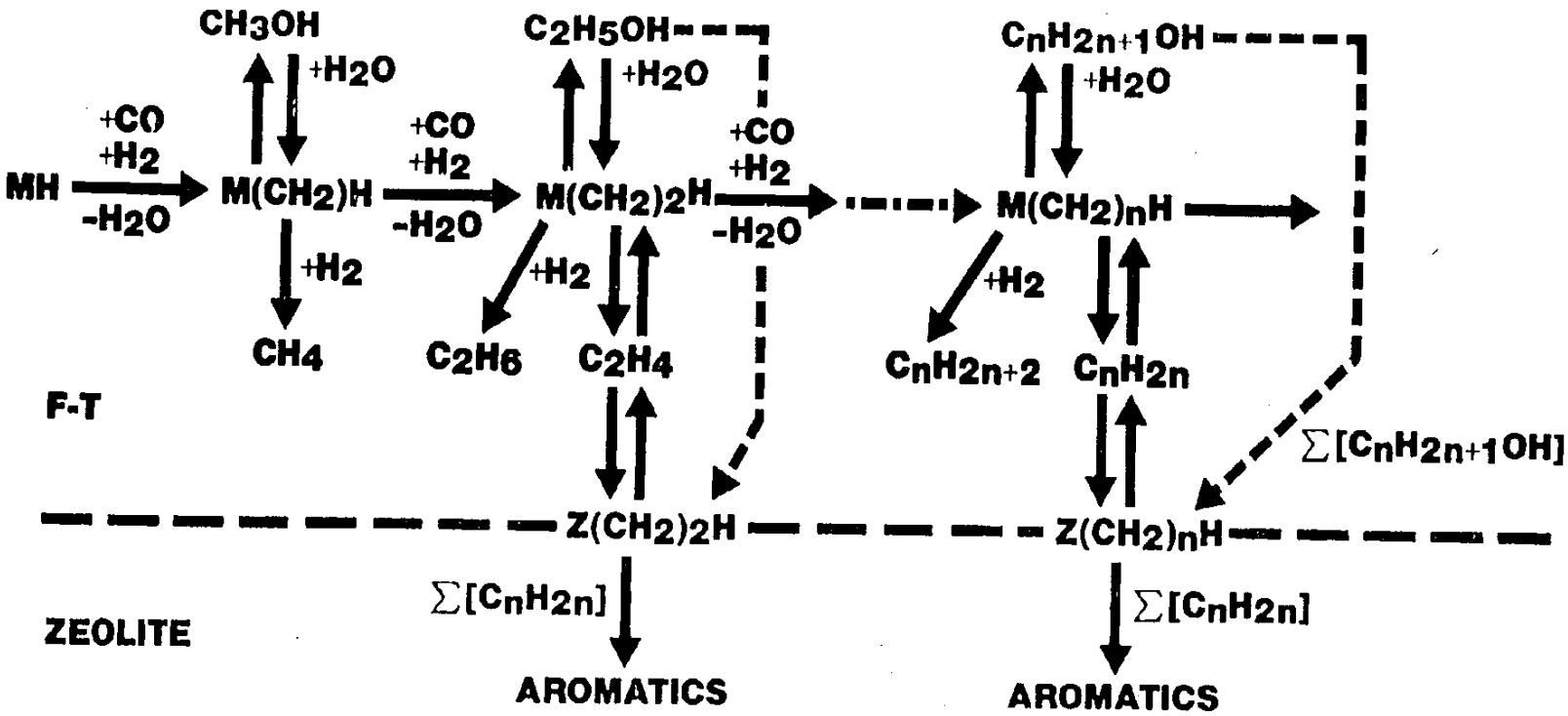
The "non-trivial polystep" reaction characteristic of bifunctional catalyst and described by Weisz and others (59) is not simply a succession of consecutive reaction steps. Rather it is two discrete sets of reaction steps, each corresponding to a particular catalyst function. These discrete sets are then linked by a stable intermediate component. Catalytica (32) has suggested that alcohols and olefins can be easily transformed into aromatic products over a ZSM-5 type zeolite catalyst. Since these components are generated from a Fischer-Tropsch catalyst, they are likely candidates for the intermediates required to link the F-T and zeolite catalyst functions.

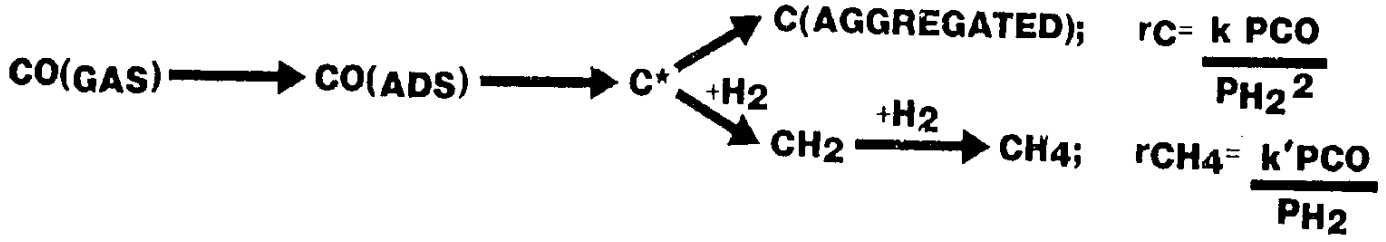
The mechanism that is suggested and which integrates these facts is shown in green in Figure 4.5-1. As before, M represents the metal site associated with the Fischer-Tropsch function, while Z represents the zeolite function. The olefin intermediate, represented by $[C_nH_{2n}]$, is shown interacting as a reversible reaction with the zeolite. In contrast, Catalytica (32) has suggested that alcohols, here represented as $[C_nH_{2n+1}OH]$, react with each other irreversibly in conjunction with the zeolite to form ketone intermediates which then can decompose to olefins. In both cases above, the olefins act as building blocks for the polymerization and cyclization reactions necessary to form aromatics on the zeolite.

The mechanism as described in Figure 4.5-1 should characterize the product structure of the bifunctional, F-T and zeolite, catalyst. The key lies in the ability of the zeolite function to intercept the components associated with the Fischer-Tropsch polymerization reaction and to convert them into aromatics.

FIGURE 4.5-1

FISCHER TROPSCH
MECHANISM IMPROVEMENTS





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