ATTACHMENT XI

Listing of Open Literature Description of Exxon FT Work

A listing of papers by Exxon personnel, and including two by E. Iglesia identified by * that were published after he left Exxon but covering work that was conducted at Exxon. The synopsis will be brief since the results and conclusions in these papers are reviewed in papers XI.1, XI.12, XI.15 and XI.26.

The polymerization of the C_1 monomer produces a distribution described by the Anderson-Schulz-Flory (ASF) distribution. Thus, each carbon number surface species has a probability of continuing the chain growth or terminating the polymerization to produce a product. The ASF mechanism assumes that the ratio of chain propagation r_p, and termination, r_t, are independent of they hydrocarbon chain length. The resulting hydrocarbon selectivity predicted is described as:

$$m_i = a \, m_{i-1} = (1 - a) \, a^{i-1} \qquad\qquad [1]$$

where m_i is the mole fraction of hydrocarbon containing i carbon atoms and a is the probability for chain growth and is related to the probability for chain growth and termination as

$$a = r_p / (r_p + r_t). \qquad\qquad [2]$$

According to the ASF mechanism, a plot of the logarithm of the mole fractions of the hydrocarbons produced versus the number of carbon atoms in the hydrocarbon should result in a straight line with a single slope given by the chain growth probability, a. Much of the data generated, both in small and large reactor systems, exhibit two values of a. Recently an explanation has been given for this deviation of the hydrocarbon selectivity from that predicted by the ASF reaction mechanism has been

offered by workers at Exxon (XI.1,XI.15,XI.18,XI.26). The explanation termed as the Transport-Enhanced Olefin Re-adsorption (TEOR) model is briefly outlined below.

The normal ASF chain growth scheme is outlined in Figure 1. This mechanism for hydrocarbon production has been modified by the Exxon workers first as shown in figure 2 and later as shown in figure 3. The modified mechanism is claimed to be applicable for iron, cobalt and ruthenium catalysts, although date for iron has not been included.

This mechanism distinguishes between paraffins and olefins formed by termination of the hydrocarbon chain on the catalyst surface. Further, the olefins formed can re-adsorb back onto the catalyst surface and re-enter the chain growth process. This process of re-adsorption is quantified by a re-adsorption rate (r_R). Finally, the olefins formed can be hydrogenated, at least partially on other catalytic sites (rate given by r_S) to paraffins. The effective rate of chain termination is then

$$r_t = r_o + r_H - r_R \qquad\qquad\qquad [3]$$

where r_o is the rate of termination to olefins and r_H is the rate of termination to paraffins. Thus olefin re-adsorption serves to decrease the effective rate of termination.

The rates of chain growth, olefin termination, paraffin termination, hydrogenation and olefin re-adsorption are assumed to be independent of chain length, i.e., the number of carbon atoms in the hydrocarbon. The value of the chain growth parameter, a, is then

$$a = r_p/(r_p + r_o + r_H - r_R) \qquad\qquad\qquad [4]$$

Note that due to the independence of the rates with chain length, this modified mechanism by itself cannot predict two or more values of the chain growth probability with increasing number of carbon atoms in the hydrocarbon.

The pores inside a catalyst particle are filled with the heavier hydrocarbon products (presumably liquid under reaction conditions) from the FTS. In the TEOR model it is assumed that this limits or exerts a strong influence on the diffusion of the FTS hydrocarbon products (both olefins and paraffins) out of the pores. The effect of diffusion resistance is to increase the time spent in a catalyst pore by the FTS hydrocarbon products. The diffusivity of individual hydrocarbons is dependent on their molecular weight or chain length or the number of carbon atoms. In the TEOR model, the dependence of diffusivity is assumed to be an exponential function of the number of carbon atoms:

$$D = D_o e^{-0.3i} \qquad\qquad [5]$$

where D_o is a constant.

As the diffusivity increases with chain length, the time spent inside a catalyst pore is longer for a hydrocarbon containing, for instance, 20 carbon atoms than for a hydrocarbon containing 10 carbon atoms. Thus the olefins containing 20 carbon atoms have a greater chance to re-adsorb on to the catalyst surface and re-enter the chain growth process than olefins containing 10 carbon atoms. Hence, the rate of re-adsorption for a C_{20} olefin is greater than the rate of re-adsorption of a C_{10} olefin, i.e., the re-adsorption rate for heavier olefins is enhanced by transport limitations. Then, according to equation [4], the probability for chain growth, a, should increase with the number of carbon atoms in the hydrocarbon.

The diffusivity of light olefins (C_2-C_{10}) in the liquid-filled catalyst pores is fairly high so that the re-adsorption rate of these olefins is relatively unaffected. Thus, a single value of the chain growth probability, a, is obtained for these hydrocarbons. For hydrocarbons containing higher than 10 carbon atoms, the rate of diffusion becomes

increasingly significant. Hence, the rate of re-adsorption, and thus the chain growth probability (a), increases with the hydrocarbon chain length. The increasing rate of olefin re-adsorption with hydrocarbon chain length finally reaches the rate of olefin termination, i.e.,

$$r_R = r_o \qquad\qquad [6]$$

at a sufficiently high value of the number of carbon atoms (C_{25} or greater) in the olefin. At this point no more olefins are desorbed from the catalyst surface and the resulting probability for chain growth becomes

$$a = r_p/r_p + r_H \text{ for } C_{25}+ \text{ olefins} \qquad\qquad [7]$$

Thus, for $C_{25}+$ hydrocarbons, the chain growth probability does not depend on the hydrocarbon length and once again approaches a constant value.

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