Chapter III

Intrinsic Rate Parameters of the Fischer-Tropsch Synthesis

ABSTRACT

Fischer-Tropsch synthesis results in a large range of products, from methane to higher hydrocarbons. Steady-state product distributions obtained during the Fischer-Tropsch synthesis can be described by the Anderson-Schulz-Flory (ASF) polymerization model. The product distribution is characterized by a single parameter, α, the probability of chain growth, which is the ratio of the apparent rate constant for propagation (k_p') to the sum of the apparent rate constant for propagation and the rate constant for termination (k_t). Expressions are derived for k_p', k_t, and the average hydrocarbon product carbon number. It is shown that steady state rate data cannot be used to evaluate k_p' and k_t individually.

The reaction mechanism of Fischer-Tropsch synthesis is viewed as a surface polymerization in which the monomer is produced *in situ* from CO and H_2 on the catalyst surface (1-3). The experimentally observed product distribution obeys Anderson-Schulz-Flory (ASF) polymerization kinetics: $N_{Cn}/N_{Cn-1} = \alpha$, where N_{Cn} is the turnover frequency of products of carbon number n and α is the chain growth parameter and is independent of chain length n. This is indicative of propagation by a sequence of independently repeated additions of a monomer group to the growing chain, in competition with the termination step.

$$C_{n-1}(s) \xrightarrow{k_p'} C_n(s) \xrightarrow{k_p'} C_{n+1}(s)$$
$$+C_1(s) \downarrow \quad +C_1(s)$$
$$C_n(g)$$

The ASF distribution can be expressed by the following two equations:

$$N_{C_n} = k(1-\alpha)^2\alpha^{n-1} \qquad (1)$$

$$\alpha = \frac{k_p'}{k_p'+k_t} \qquad (2)$$

where k is a rate parameter and $k_p' = k_p\theta_m$, k_p being the intrinsic propagation rate and θ_m the coverage of the monomer building block. N_{Cn}, α and k can be determined from steady-state data. The objective is to derive individual expressions for k_p' and k_t.

N_{CO} can be expressed in terms of the turnover frequency for producing a product with n carbon atoms, N_{Cn}, in the following

manner.

$$N_{CO} = \sum_{n=1}^{\infty} nN_{C_n} \qquad (3)$$

Kellner and Bell (4) have shown that N_{Cn} can be expressed as

$$N_{C_n} = k_t\theta_n \qquad (4)$$

where θ_n is the surface coverage by chains containing n carbon atoms. If chain growth occurs by the addition of single carbon units, it then follows that

$$\theta_n = \theta_1\alpha^{n-1} \qquad (5)$$

Now, the average product carbon number, n_{av} is given by the following expression:

$$n_{av} = \frac{\sum_{n=1}^{\infty} nN_{C_n}}{\sum_{n=1}^{\infty} N_{C_n}} \qquad (6)$$

Substitution of eqns. 3 and 4 into eqn. 6 results in

$$n_{av} = \frac{N_{CO}}{k_t \sum_{n=1}^{\infty} \theta_n} \qquad (7)$$

By substitution of eqns. 7 and 8 into eqn. 9, it can be shown that

$$n_{av} = \frac{\sum_{n=1}^{\infty} n\alpha^{n-1}}{\sum_{n=1}^{\infty} \alpha^{n-1}} \qquad (8)$$

and for $\alpha < 1$, this simplifies to

$$n_{av} = \frac{1}{(1-\alpha)} \qquad (9)$$

Using eqns. 7 and 9 in conjunction with eqns. 1 and 2, it can further be shown that

$$k_t = \frac{k(1-\alpha)}{\sum_{n=1}^{\infty} \theta_n} \qquad (10)$$

and

$$k_p' = \frac{k\alpha}{\sum_{n=1}^{\infty} \theta_n} \qquad (11)$$

Evaluation of k_p' and k_t requires determination of the sum of the surface coverages of the precursors to the gas-phase hydrocarbon products. It is evident from the above analysis that steady state rate data cannot be used to evaluate k_p' and k_t despite claims to have done so (5,6), since such data do not provide the sum of surface coverages appearing in the denominator of eqns. 10 and 11. As has already been noted by Zhang and Biloen (7), k_p' and k_t can be properly evaluated from transient isotopic tracer experiments.

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