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LETTERS TO THE EDITORS

Comments on "Evaluation of the Intrinsic Rate Parameters of the Fischer–Tropsch Synthesis"

In a recent paper, Adesina (*1*) has claimed that it is possible to calculate the rate constant for chain propagation, k_p, and the rate constant for chain termination, k_t, for Fischer–Tropsch synthesis from steady-state rate data. It is stated that this can be done using

$$r_n = k(1 - \alpha)^2 \alpha^{n-1} \tag{1}$$

$$\alpha = \frac{k_p}{k_p + k_t} \tag{2}$$

$$n_{av} = N_{CO} \times t_{HC} \tag{3}$$

or

$$n_{av} = \frac{N_{CO}}{k_t} \tag{3a}$$

$$k_t = k \frac{(1 - \alpha)}{m_{Co}} \tag{4}$$

$$k_p = k \frac{(\alpha)}{m_{Co}}, \tag{5}$$

where r_n is the formation rate of hydrocarbon with carbon number n; α is the probability of chain growth; k is a rate parameter; n_{av} is the average carbon number; N_{CO} is the turnover frequency for CO consumption to form hydrocarbons; t_{HC} is the hydrocarbon residence time $(1/k_t)$; and m_{Co} is the metal catalyst surface concentration (Co is the metal used in this study). α and k can be determined from steady-state data and hence the author contends that k_p and k_t can be evaluated using Eqs. (4) and (5). The purpose of this letter is to show that Eqs. (3)–(5) are incorrect, and k_p and k_t cannot be determined from steady-state data.

We begin by recognizing that N_{CO} can be expressed in terms of the turnover frequency for producing a product with n carbon atoms, N_{C_n}, in the following manner:

$$N_{CO} = \sum_{n=1}^{\infty} n N_{C_n}. \tag{6}$$

Kellner and Bell (*2*) have shown that N_{C_n} can be expressed as

$$N_{C_n} = k_t \theta_n, \tag{7}$$

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

$$\theta_n = \theta_1 \alpha^{n-1}. \tag{8}$$

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

$$n_{av} = \frac{\sum_{n=1}^{\infty} n N_{C_n}}{\sum_{n=1}^{\infty} N_{C_n}}. \tag{9}$$

Substitution of Eqs. (6) and (7) into Eq. (9) results in

$$n_{av} = \frac{N_{CO}}{k_t \sum_{n=1}^{\infty} \theta_n}. \tag{10}$$

Comparison of Eqs. (3a) and (10) shows that the factor involving the sum of the surface hydrocarbon coverages is missing in Eq. (3a). By substitution of Eqs. (7) and (8) into Eq. (9), it can be shown that

$$n_{av} = \frac{\sum_{n=1}^{\infty} n\alpha^{n-1}}{\sum_{n=1}^{\infty} \alpha^{n-1}} \tag{11}$$

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

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$$n_{\mathrm{av}} = \frac{1}{(1-\alpha)}. \tag{12}$$

Using Eqs. (10) and (12) in conjunction with Eqs. (1) and (2), it can further be shown that

$$k_{\mathrm{t}} = \frac{k(1-\alpha)}{m_{\mathrm{Co}} \sum_{n=1}^{\infty} \theta_n} \tag{13}$$

and

$$k_{\mathrm{p}} = \frac{k\alpha}{m_{\mathrm{Co}} \sum_{n=1}^{\infty} \theta_n}. \tag{14}$$

It is evident from the above analysis that steady-state rate data cannot be used to evaluate k_{p} and k_{t} since such data do not provide the sum of surface coverages appearing in the denominator of Eqs. (13) and (14). Consequently, evaluation of k_{p} and k_{t} from Eqs. (4) and (5) will result in erroneous values for these parameters. The flaw in deriving Eqs. (4) and (5) in Adesina's work (*1*) is the use of Eq. (3a) (3), which was taken from Fu and Bartholomew (*3*). As has already been noted by Zhang and Biloen (*4*), k_{p} and k_{t} can be properly evaluated from transient isotopic tracer experiments.

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