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Evaluation of the Intrinsic Rate Parameters of the Fischer–Tropsch Synthesis

In spite of the multiplicity of proposals available in the literature on the mechanism of hydrocarbon formation during the Fischer–Tropsch reaction, it is generally conceded that the synthesis is a polymerization reaction (*1*). Thus, the steady-state product distribution is commonly represented by the Anderson–Schulz–Flory (ASF) model,

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

where r_n is the formation rate of hydrocarbon with carbon number, n; α is the chain growth factor; and k is the rate parameter.

The growth factor α, is further defined as

$$\alpha = \frac{r_p}{r_p + r_t}, \qquad (2a)$$

where r_p is the propagation rate and r_t is the termination rate. Although α may be easily computed from a fit of the rate data to the linearized version of the ASF model (cf. Eq. (14)), it has not been possible to estimate the individual values of r_p and r_t from steady-state kinetic data. We wish to demonstrate in this note that in the spirit of Vannice's philosophy (*2*) (strong advocation of the use of specific activity or turnover frequency rather than global rate in the discussion of kinetic studies), it is possible to obtain the intrinsic kinetic parameters k_p and k_t from steady-state data, where

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

and k_p is the propagation frequency (r_p/m_{Co}), k_t is the termination frequency (r_t/m_{Co}), and m_{Co} is the metal catalyst surface concentration, cobalt sites per gram catalyst.

Additionally, the effect of feed composition on each of these decoupled parameters is examined. We also remark on how insights gained from such examination may help in formulating optimal catalyst recipes.

The rate data utilized in this study were collected from an experimental rig fully described elsewhere (*3*). On the basis of hydrogen chemisorption measurements, the kieselguhr-supported chemical cobalt catalyst gave a surface concentration of 29.82 micromole cobalt per gram of freshly reduced catalyst.

According to Fu and Bartholomew (*4*), the average carbon number, $\bar{n}$, is given by

$$\bar{n} = \mathrm{TOF}_{CO} \times t_{HC}, \qquad (3)$$

where TOF_{CO} is the turnover frequency for carbon monoxide and t_{HC} is the hydrocarbon residence time ($1/k_t$).
However,

$$\mathrm{TOF}_{CO} = \frac{\text{moles of CO consumed per gram cat. per s}}{\text{cobalt sites per gram cat.}}$$

or

$$\mathrm{TOF}_{CO} = \frac{r_{CO}}{m_{Co}} \qquad (4)$$

and

$$t_{HC} = \frac{m_{Co}}{r_t}. \qquad (5)$$

Combining Eqs. (4), (5), and (3) gives

$$\bar{n} = \frac{r_{CO}}{r_t} \qquad (6)$$

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but

$$r_{\mathrm{CO}} = \text{rate of CO converted to hydrocarbon} + \text{rate of } \mathrm{CO_2} \text{ production.} \qquad (7)$$

Under the experimental conditions used, CO_2 was not detected on an on-line IR 702 digital spectrophotometer (*5*); thus,

$$r_{\mathrm{CO}} = \text{rate of CO converted hydrocarbon} = \sum_{n=1}^{\infty} n r_n. \qquad (8)$$

Using Eq. (1) in Eq. (8)

$$\sum_{n=1}^{\infty} n r_n = k(1 - \alpha)^2 \sum_{n=1}^{\infty} n \alpha^{n-1}. \qquad (9)$$

Recall that

$$\sum_{n=0}^{\infty} \alpha^n = \frac{1}{(1 - \alpha)} \quad \text{if } \alpha < 1. \qquad (10)$$

Then

$$\frac{\partial}{\partial \alpha}\left(\sum_{n=0}^{\infty} \alpha^n\right) = \sum_{n=1}^{\infty} n \alpha^{n-1} = (1 - \alpha)^{-2}. \qquad (11)$$

Substituting Eq. (11) into Eq. (9), we obtain

$$r_{\mathrm{CO}} = \sum_{n=1}^{\infty} n r_n = k \qquad (12)$$

and

$$\bar{n} = \frac{k}{r_{\mathrm{t}}}. \qquad (13)$$

Fortunately, k is easily obtained from the intercept of the ASF plot ($\ln r_n$ vs n) described by

$$\ln r_n = \ln\left\{k \frac{(1 - \alpha)^2}{\alpha}\right\} + n \ln \alpha. \qquad (14)$$

We note that

$$\bar{n} = \frac{1}{(1 - \alpha)} \qquad (15)$$

and Eq. (13) rearranges to

$$r_{\mathrm{t}} = k(1 - \alpha) \qquad (16a)$$

whereupon, from Eq. (2a),

$$r_{\mathrm{p}} = \alpha k \qquad (16b)$$

and

$$k_{\mathrm{t}} = k \frac{(1 - \alpha)}{m_{\mathrm{Co}}} \qquad (17a)$$

$$k_{\mathrm{p}} = \frac{\alpha k}{m_{\mathrm{Co}}} \qquad (17b)$$

The k values reported in Table 1 at the seven feed compositions were evaluated from a least-squares fit of the rate data to Eq. (14). Only the C_3 to C_9 data were used because the C_2 rates tend to deviate from the ASF prediction.

As may be seen from Fig. 1, the optimal chain growth factor and carbon number are found between an H_2:CO ratio of 1:3 to 1:1, the values being 0.68 and 3.0, respectively. It may be pointed out that the reported values of α in the literature (*1*) vary considerably depending on the type of catalyst, temperature, pressure, and conversion. While Pichler and Schulz (*6*) obtained growth factor of 0.8 for a cobalt catalyst for a feed containing 33% CO at 1 atm and 458 K, Everson *et al.* (*7*) observed values of 0.65–0.73 for ruthenium catalyst at 523 K. In fact, an increase in temperature may give rise to a drop in chain growth factor. In addition, when conversions are high, the inclusion of C_{10+} hydrocarbons in the ASF plot leads to greater values of α. It is there-

TABLE 1

Values of ASF Constants at Different Feed Compositions

y_{H_2}	α	k (micromol./gcat · s)
0.10	0.43	0.0733
0.24	0.67	0.2450
0.50	0.68	0.6090
0.75	0.61	0.9300
0.83	0.60	1.1600
0.90	0.56	1.1200
0.95	0.44	1.0600

Note. Experimental conditions: pressure = 110 kPa; temperature = 473 K.

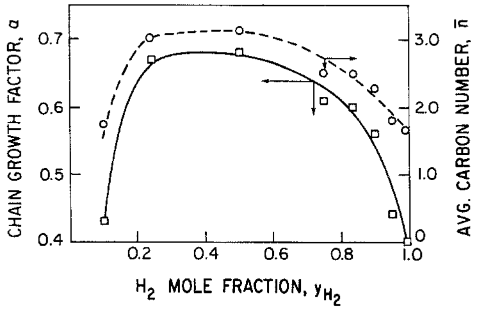

FIG. 1. Effect of feed composition on α and $\bar{n}$.

fore not surprising that with the differential conversion (<10%) used in this study, in concert with a temperature of 473 K, the growth factor values are lower than those obtained by Pichler and Schulz (*6*). Figure 2 shows the variation in the propagation frequency and hydrocarbon residence time on the catalyst surface with respect to feed composition. Intriguingly, the conditions which promote optimal propagation also favor the least hydrocarbon residence time on the catalyst. Mere inspection of Eq. (2b) reveals that the ideal catalyst ($\alpha \rightarrow 1$) would be that for which the conditions for maximum propagation frequency coincide (or at least near so) with the maximum hydrocarbon residence time (minimum termination frequency).

In search for an ideal catalyst, it is perhaps instructive to establish a relationship (probably empirical) between each of these two intrinsic kinetic parameters and such innate catalyst properties as, dispersion, percent loading, composition, and metal particle size. Studies by Nijs and Jacobs (*8*) and Reuel and Bartholomew (*9*) actually indicate that α is strongly sensitive to these catalytic properties. Since it is now possible to decouple the two constituent kinetic parameters in α, an immediate extension of the type of study reported in (*8*) and (*9*) to k_p and k_t rather than α is self-evident. Consequently, the individual (rather than collective) dependency of k_t and k_p on these properties may be established.

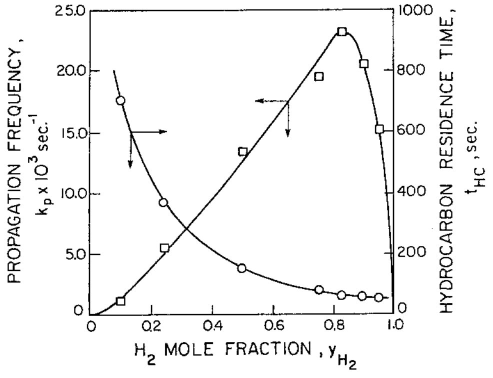

FIG. 2. Effect of feed composition on k_p and t_{HO}.

Intuitively, information from such investigation may enable the catalyst designer to prepare recipes in which one of these parameters is significantly altered in a favored direction without a corresponding detrimental shift in the other.

In conclusion, we remark that although Zhang and Biloen (*10*) have shown that it is only possible to estimate k_p and k_t from isotopic transient measurements, our analysis permits the usage of steady-state data for such estimation. Lack of Arrhenius parameters and values for k (from Ref. (*10*)) forbids a direct comparison of our results (at 473 K) with theirs (at 483 K). Even so, parameter estimates from both studies are of the same order of magnitude.

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