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Response to Comments by Yokomizo *et al.*

In a previous letter, Yokomizo *et al.* (*1*) disagreed with the conclusions in our previous paper (*2*) on the usage of steady-state data for the procurement of the intrinsic rate parameters of the Fischer–Tropsch (FT) reaction. While it is readily admitted that isotopic transient experiments offer more information on the elementary rate processes during chemical reaction than steady-state runs, the objective of (*2*) was to provide a means of *fully* utilizing steady-state data in a manner complementary with the results obtained from other experimental techniques.

Specifically, Yokomizo *et al.* (*1*) argued that the derived expressions between k_p and k_t (propagation rate and termination rate constant, respectively) and the Anderson–Schulz–Flory (ASF) model parameters are incorrect because they were based on the relation provided in Fu and Bartholomew (*3*), namely,

$$\bar{n} = \mathrm{TOF_{CO}} \times t_{\mathrm{HC}}, \qquad (1)$$

where the parameters are as defined in (*2*). The underlying basis for Eq. (1) as discussed in (*3*) is still incontrovertible even in the face of accumulated experimental data. This is probably why Yokomizo *et al.* did not show where and why it is in "error." It would be largely repetitious and frivolous to reestablish the validity of Eq. (1). Following Eq. (1), the successive steps culminating in the final expressions for k_p and k_t (cf. Ref. (*2*)) are transparently straightforward and internally consistent.

The major point of contention seems to be the use of Eq. (3) in Ref. (*2*) vis-à-vis Eq. (7) in Ref. (*1*). It is precisely at this juncture that one sees a difficulty. No matter which FT mechanism one adopts, the rate of production of a given carbon number, r_{C_n}, and by implication, N_{C_n}, is given by

$$r_{C_n} = r_{C_{no}} + r_{C_{np}}, \qquad (2)$$

where $r_{C_{np}}$ and $r_{C_{no}}$ are the production rate for paraffin and olefin, respectively, in agreement wih Professor Bell's previous review (*4*). Unfortunately, Eq. (7) in Ref. (*1*) is merely the contribution due to olefin production. For completeness, an additional term representing paraffin contribution must be added to the RHS of Eq. (7); thus,

$$N_{C_n} = k_t\theta_n + k_t\theta_n\theta_{H_2}^m, \qquad (3)$$

where one may even further make a distinction between the termination rate constant, k_t, for both paraffin and olefin and m is 1 or 2 depending on whether H_2 is molecularly or dissociatively adsorbed. Suggesting that paraffin production is influenced by the concentration of hydrogen adatoms (second term of the RHS in Eq. (3)) is not contentious (*4–6*). Clearly, using Eq. (7) in Ref. (*1*) introduces more complications than one might at first suppose. Nor is this all. There is a fundamental problem with the use of Eqs. (13) and (14) in Ref. (*1*) with transient data. Both k and α are parameters from the ASF model and cannot be meaningfully obtained from (or used for) transient data analysis since the ASF model presupposes a steady-state concentration of surface species (Storch *et al.* (*7*)). Of course, this assumption is invalid for isotopic transient experiments. Certainly, the analysis provided in (*2*) and the attendant conclusions are still meritorious.

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