Response to "Comment on the Model for Isothermal Oscillations of Ethylene Oxidation on Platinum"

Hsueh-Chua Chang and Mobolaji Aluko (1) report that the model proposed to describe isothermal rate and oxygen activity oscillations during ethylene oxidation on platinum (2, 3) does not properly predict oscillations. They suggest that the oscillations generated by Eqs. (22–25) in Ref. (3) are artifacts which result from numerical difficulties in the integration of these equations. Their objections can be refuted both on mathematical and physical grounds. However, their and our calculations have suggested that a lower bound exists on the permissible integration step size if the model is to simulate an "infinitely fast" phenomenon, such as unstable PtO_x decomposition, with a finite-rate expression ($\alpha N_4 x_2 \theta_2$ in Eqs. (22) and (25) of Ref. (3)), however large (but finite) N_4 might be.

The authors of Ref. (1) assigned arbitrary values to the model parameters ($N_1 = N_2 = N_3 = 1, N_5 = N_6 = 0.1, N_4 = N_7 = 200$) and integrated using the Euler method with an integration step, δt, of the order of 10^{-5} times the residence time. They found that the oscillation period and amplitude vanish as the integration step size approaches zero. Additional calculations that we performed have confirmed this phenomenon, as shown in Figs. 1a and b. However, the authors of (1) failed to observe two very important facts. First, for a sufficient increase in the step size, the limit cycle amplitude and period attain constant values, independent of δt and N_4 (Figs. 1a and b). Second, for any fixed step size, an increase in N_4 causes the amplitude and period to increase and reach their δt-independent values. Such an increase in N_4 is justified because the corresponding term in the model represents an infinitely fast process step. Our calculations show that the period and amplitude increase linearly with δt up

to their limiting values (see Appendix for proof). The calculations we reported in (3) were performed for $N_4 = \infty$ (e.g., step-changes in θ_2 and x_2 when the oxide becomes unstable) and, therefore, are independent of the size of the integration step. Further mathematical discussion is given in the Appendix.

Physically, the limiting values of the oscillation period and amplitude result from the rapidity of the decomposition of the oxide relative to the mixing time in the reactor. The oxide decomposes completely before the catalytic surface senses a shift in the gas-phase composition back into the stable-oxide region. Thus, the depth of the excursion into the stable-oxide region during each cycle depends on the space velocity and amount of oxide formed in the previous limit cycle. The period of the oscillations additionally depends on the local values of the rates r_1 and r_2, as discussed in detail in (3) (Fig. 11 of Ref. (3) and related discussion).

Because Eqs. (22)–(25) of (3) describe a CSTR, the integration-step size is analogous to the mixing time in the reactor. Therefore, care must be exercised in choosing δt large enough to assure that the assumption of a well-mixed reactor is valid throughout the integration. A δt of order 10^{-5} times the residence time, as used in (1), implies a mixing time of order 10^{-5} s, which is physically unrealistic. The choice of δt is especially critical in the integration of Eqs. (22)–(25) of (3) due to the high rate of oxide decomposition and reaction. If N_4 is not taken as infinitely large, the integration of the equations is only valid if $\delta t > N_6/6N_4 x_2^c$, where x_2^c characterizes the point of the limit cycle at the stability limit. In chosing the proper value of N_4 it suffices, on physical grounds, that the reaction time
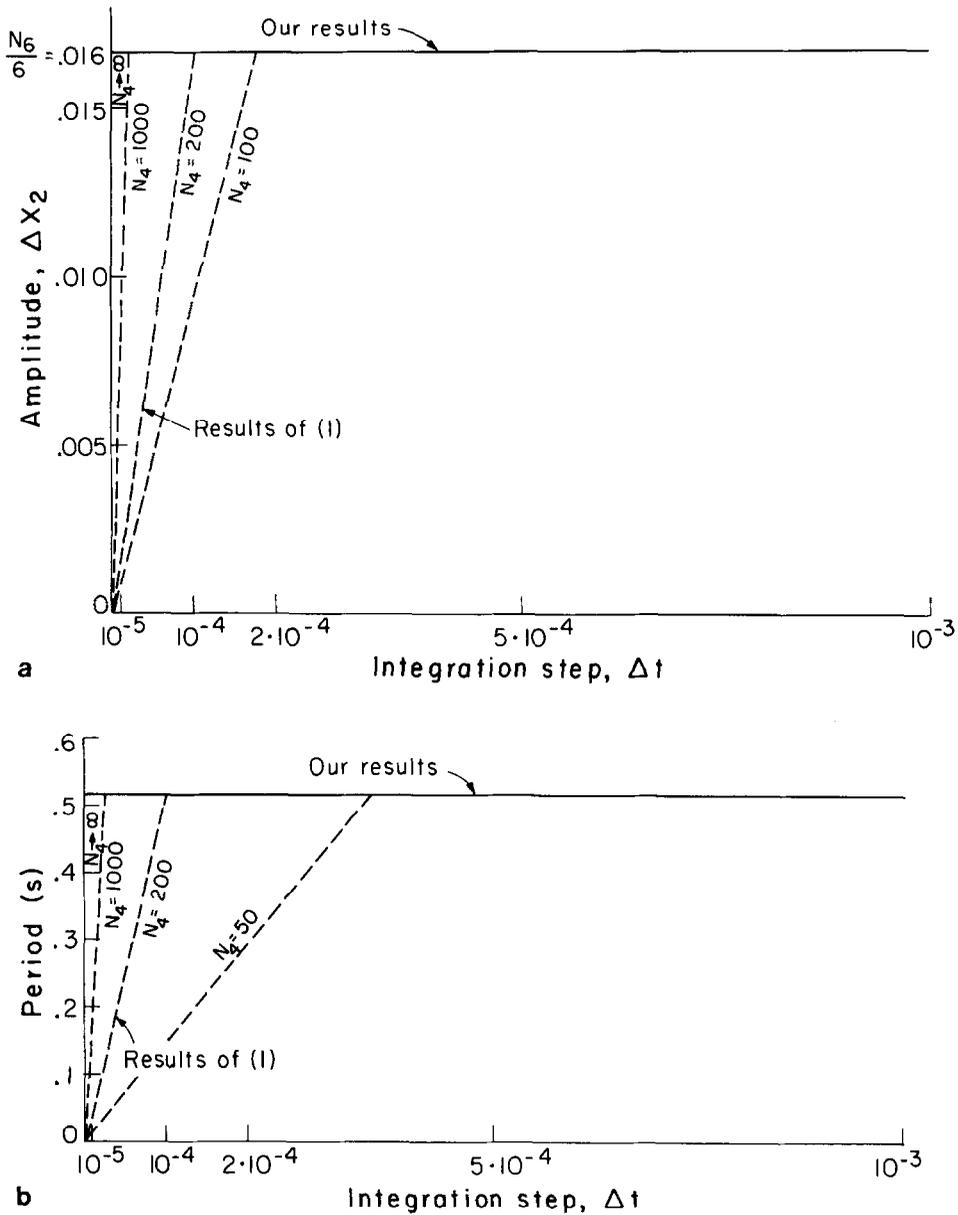
FIG. 1. Results of numerical integration of the model (3) with the conditions specified in Ref. (*1*). Effect of N_4 on limit cycle amplitude (a) and period (b).

for oxide decomposition and reaction with ethylene (proportional to $1/N_4$) and the mixing time in the reactor must be of the same magnitude. This is physically reasonable, as both are diffusion-limited processes.

   The mathematical arguments presented in (*1*) also fail to support the authors' objections to our model. To the "right" of the stability line (or surface) $\theta_2 = 0$ because in this region the oxide is unstable. Consequently the vector normal to this surface and pointing to the "right" is equal to $\hat{n}^T = [-1, K^*, 0, \beta]/(1 + K^{*2} + \beta^2)^{1/2}$, where β is

any nonpositive number. Furthermore, as we approach the stability line from the "right" ($\alpha = 1$), $\mathbf{f} \cdot \hat{\mathbf{n}}$ is *always* greater than zero because θ_2 is zero *de facto*. When we approach the stability line from the "left," Eq. (5) of (*1*) is correct just *before* the trajectory arrives at the oxide stability limit. When it does arrive at the stability limit, α changes from 0 to 1 while θ_2 is still nonzero. The large value of N_4 causes $\mathbf{f} \cdot \hat{\mathbf{n}}$ to switch from a positive to a negative value, thus initiating the limit cycle. When integrating Eqs. (22)–(25) of (*3*) exactly (e.g., $\delta t \to 0$), the physical requirement that the oxide decomposition and reaction time and the mixing time be of equal magnitude translates into a mathematical requirement that $N_4 \to \infty$. That is, when the stability limit is reached from the left, $\mathbf{f} \cdot \hat{\mathbf{n}} \to -\infty$, thereby initiating a finite limit cycle. Perhaps a mathematically more formal way to visualize the above discussion is to represent the infinitely fast decomposition step in Eqs. (23) and (25) of (*3*) by a Dirac function of the form $\delta(x_1 - K^* x_2)\theta_2$, instead of the term $\alpha N_4 x_2 \theta_2$ used originally.

It should be noted that it is necessary to assume an "infinitely fast" oxide decomposition and reaction step *only if* one insists upon assuming infinitely small mixing time in the reactor; i.e., $\delta t = 0$.

The authors of (*1*) are correct in noting that if $N_3 > 1/K^*$ and the initial condition lies to the left of the stability limit then the model predicts oscillations. The oscillations do not resemble a second steady state, as discussed above. The model also predicts that no oscillations should occur when $1/3 < N_3 < K^*$ and both the steady-state and initial condition lie to the right of the stability limit. These predictions have not been verified experimentally due to the difficulty in imposing the necessary true step changes in concentrations.

In conclusion, the model presented in (*3*) has been shown to be physically and mathematically valid. The integration of the pertinent equations is nontrivial and requires a firm physical understanding of the reactor dynamics. Further refinements in the model would certainly be useful, as described in (*3*). However, the model in its present form successfully describes all steady-state and oscillatory experimental behavior in a semi-quantitative fashion.

APPENDIX

Here, we prove the following three additional points related to the mathematical model presented in (*3*).

(a) The integration step δt in the Euler algorithm should be larger than

$$\frac{N_6}{6N_3} \cdot \frac{(3 - K^*)}{(3N_3 - 1)}$$

for the accurate calculation of the periodic phenomena taking place near the oxide stability line.

(b) The oscillation amplitude $|\Delta x_2|$ is given by $\Delta x_2 = N_6/6$.

(c) When condition (a) is violated, the amplitude is given by

$$\Delta x_2 = N_4 \frac{(3N_3 - 1)}{(3 - K^*)} (\delta t).$$

Proof. Let t_0, x_1^o, x_2^o, θ_1^o, θ_2^o, denote the time and the value of x_1, x_2, θ_1, θ_2 when the trajectory meets the oxide stability line as it tries to go from the "left" to the "right." Then α changes from 0 to 1, oxide starts to decompose, and the N_4 terms dominate the corresponding Eqs. (23) and (25) of Ref. (*3*). Consequently,

$$\Delta x_2 = -N_4 x_2^o \, \delta t, \qquad \text{(A1)}$$

$$\Delta \theta_2 = -\frac{6N_4}{N_6} x_2^o \, \delta t, \qquad \text{(A2)}$$

$$\Delta x_2 = \frac{N_6}{6} \Delta \theta_2, \qquad \text{(A3)}$$

where δt is the integration step in the Euler method. Because of the large value of N_7, we can accurately approximate that $\theta_2(t_0^-) = 1$. At $t_0 + \delta t$ the trajectory will be moved to the left of the stability line and α will change back to 0, allowing new oxide to form. Physically this is not possible un-

less *all* the previously existing oxide decomposed and the liberated oxide reacted with ethylene. It then follows that δt should be large enough to make $\Delta\theta_2 = -1$, hence

$$\delta t \gtrsim \frac{N_6}{6N_4 x_2^\circ} \quad \text{and} \quad |\Delta x_2| = \frac{N_6}{6}. \quad \text{(A4)}$$

If δt is smaller than the above value only part of the oxide decomposes before new oxide is formed and naturally the oscillation amplitude, which is given by Eq. (A1) above, depends linearly on the step size δt, as shown in Fig. 1a.

We further assume that x_2° lies close to the stoichiometry line, $x_1 = 3x_2 + 1 - 3N_3$. This assumption has been motivated by observation of the numerical results reported in (*3*). It then follows that

$$x_2^\circ = \frac{3N_3 - 1}{3 - K^*}. \quad \text{(A5)}$$

Then Eq. (A4a) transforms to

$$\delta t \gtrsim \frac{N_6}{6N_4} \frac{(3 - K^*)}{(3N_3 - 1)} \quad \text{and} \quad \delta x_2 = \frac{N_6}{6} \quad \text{(A6)}$$

and if the first is not satisfied, then according to (A1), the amplitude is given by

$$|\Delta x_2| = N_4 \frac{3N_3 - 1}{3 - K^*} \delta t. \quad \text{(A7)}$$

REFERENCES

1. Chang, H.-C., and Aluko, M., *J. Catal.* **73**, 198 (1981).
2. Vayenas, C. G., Lee, B., and Michaels, J., *J. Catal.* **66**, 36 (1980).
3. Vayenas, C. G., Georgakis, C., Michaels, J., and Tormo, J., *J. Catal.* **67**, 348. (1981).

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