JOURNAL OF CATALYSIS 73, 198–200 (1982)

LETTERS TO THE EDITORS

Comment on the Model for Isothermal Oscillations of Ethylene Oxidation on Platinum

INTRODUCTION

Vayenas *et al.* (*1*) have recently proposed a model to explain the occurrence of limit cycles during the oxidation of ethylene on a platinum catalyst, which was reported in an earlier paper (*2*). In their experimental studies, the activity of oxygen on the catalyst surface is monitored by solid electrolyte potentiometry (SEP) and limit cycles are found to occur only over a well-defined range of surface oxygen activity. From this and other experimental observations, they postulate the existence of a second site type on which a surface platinum oxide PtO_x is formed, in addition to a first site type which produces reactive dissociatively chemisorbed oxygen. The thermodynamic stability of this oxide is dependent on the ratio of the reactant partial pressures P_{O_2}/P_{Et}, and it is this stability characteristic which provides a switching mechanism that is the basis for the oscillations. The resulting model equations are then shown to produce oscillations that resemble the experimental data. Frequency dependence on inlet ethylene/oxygen ratio N_3 and residence time θ from the model are shown to be in satisfactory agreement with the experimental data.

While we agree with the authors that catalytic activity variations due to the thermodynamic stability of a new phase may be the key mechanism for oscillations in their system and other oxidation reactions on noble metals, we have discovered that their mathematical model does not actually produce observable limit cycles. Consequently the oscillations they reported are purely numerical illusions.

DISCUSSION

The relevant governing equations are Eqs. (22)–(25) of Ref. (*1*), and their corrected version (a number of typographical errors occur in the original set) are as follows:

$$\begin{aligned}
\dot{x}_1 &= 1 - x_1 - \tfrac{1}{2}N_1x_1(1-\theta_1) - \tfrac{5}{2}N_2x_2\theta_1,\\
\dot{x}_2 &= N_3 - x_2 - N_2x_2\theta_1 - \alpha N_4x_2\theta_2,\\
N_5\dot{\theta}_1 &= N_1x_1(1-\theta_1) - N_2x_2\theta_1\\
&\qquad - (1-\alpha)N_7\theta_1(1-\theta_2),\\
N_6\dot{\theta}_2 &= (1-\alpha)N_7\theta_1(1-\theta_2) - 6\alpha N_4x_2\theta_2,
\end{aligned} \tag{1}$$

where

$$\begin{aligned}
\alpha &= 0 \quad \text{if } x_1/x_2 > K^*(T),\\
&= 1 \quad \text{if } x_1/x_2 < K^*(T).
\end{aligned} \tag{2}$$

We shall denote Eq. (1) by the vector notation:

$$\dot{\mathbf{y}} = \mathbf{f}. \tag{3}$$

Let the unit normal of the stability surface defined by $x_1/x_2 = K^*$ in the $(\mathbf{x}, \boldsymbol{\theta})$ phase space be denoted $\hat{n}$. This unit vector is defined to point to the "right" of the surface in the direction of decreasing x_1. Consequently,

$$\hat{n} = \frac{1}{(1+K^{*2})^{1/2}}\begin{pmatrix}-1\\K^*\\0\\0\end{pmatrix}. \tag{4}$$

Now according to the model, as soon as the system trajectory crosses the stability surface from x_1/x_2 less than K^* to the other side (in the direction of $-\hat{n}$), α instantaneously switches from 1 to 0. Thus if

0021-9517/82/010198-03$02.00/0
Copyright © 1982 by Academic Press, Inc.
All rights of reproduction in any form reserved.

$$\mathbf{f} \cdot \hat{\mathrm{n}} > 0 \qquad \text{for } \alpha = 0 \qquad (5)$$

in the "left" neighborhood of the stability surface, then the system trajectory can spend only an infinitesimal amount of time on the $\alpha = 0$ side of the stability surface before it is sent back to the $\alpha = 1$ side. Since the numerical results of Vayenas *et al.* (*1*) claim that the oscillations are almost entirely in the $\alpha = 0$ region, confirmation of inequality (5) is sufficient to refute their results.

Setting α to zero, substituting Eqs. (1) and (4) into expression (5) and setting $x_1 = K^*x_2$, one obtains:

$$f \cdot \hat{n} = \frac{1}{(1 + K^{*2})^{1/2}}[(-1 + K^*N_3) + N_2x_2\theta_1(\tfrac{5}{2} - K^*) + \frac{N_1}{2}K^*x_2(1 - \theta_1)]. \qquad (6)$$

In the range of temperatures studied (200–400°C), K^* never exceeds $\frac{5}{2}$. Moreover θ_1 is restricted between 1 and 0, which must be true physically as well as because the system trajectories of Eq. (1) can be mathematically shown to be limited in this range of θ_1 if it begins within the same range. Consequently the last two terms within the square brackets in Eq. (6) are both positive, and thus a sufficient condition for inequality (5) to hold is:

$$K^*N_3 > 1. \qquad (7)$$

However, inequality (7) violates the first of the following two conditions claimed by Vayenas *et al.* to be sufficient conditions for model-predicted oscillations, namely,

C1: $\frac{1}{3} < N_3 < 1/K^*$.

C2: The steady state of the system, Eqs. (1) (which depends on N_1, N_2, N_3) lies below the oxide stability surface $x_1 = K^*x_2$.

Consequently the determination of the sign of $\mathbf{f} \cdot \hat{n}$ in Eq. (6) requires consideration of all the terms, and in general no a priori determination is evident. Nevertheless, even for parameter values that enable conditions C1 and C2 to be satisfied, our numerical results have shown that finite oscillations do not occur on *either* side of the stability surface. This fact can be explained by noting first that due to the magnitude of N_4, we have found that the system always satisfies the inequality

$$\mathbf{f} \cdot \hat{n} < 0 \qquad \text{for } \alpha = 1 \qquad (8)$$

in the immediate "right" neighborhood of the stability surface. Consequently, when both inequalities (5) and (8) are ture, the oscillations are then restricted to the stability surface with zero amplitude in x_1 and x_2 and zero period, thus the limit cycle is an infinitesimally small one which is, in essence, a locally stable steady state. These facts are verified in the next section.

NUMERICAL RESULTS

Our explanation for the numerical results reported by Vayenas *et al.* (*1*) is that in their Euler numerical scheme, large time step sizes were chosen such that the trajectory marched deep into the $\alpha = 0$ side in one single step. Hence an observed oscillation cycle actually consists of this single step and the return path of the system trajectory. This is clearly a numerical aberration (since how "deep" will always depend on the step size chosen) and explains the difficulty the authors encountered in the use of the Runge–Kutta method (*1*). Our own attempt to employ the IBM IMSL integration routine DGEAR (in which step sizes are automatically varied as required) failed to produce any oscillations.

More importantly, if the Euler scheme is used, the amplitudes and the period should reduce with decreasing step size. This is confirmed in Table 1, where the results of integrating Eq. (1) with the given parameter values are presented. (Vayenas *et al.* did not give the actual parameter values used in their integrations. Representative values are thus chosen for this study.) These parameter values satisfy the sufficient conditions of Vayenas *et al.* for oscillations (con-

TABLE 1

Dependence of Amplitude and Period on Step Size of an Euler Numerical Scheme. $N_1 = N_2 = N_3 = 1$, $N_4 = N_7 = 200$, $N_5 = N_6 = 0.1$, $K^* = 0.6$

Step size ($\times 10^5$)	Amplitude		Period
	x_1	x_2	
10.0	0.0029	0.0151	0.16
5.0	0.0006	0.0063	0.07
2.5	0.0002	0.0032	0.05
1.0	0.	0.001	0.04

ditions C1 and C2). Note from Table 1 that both amplitude and period approach zero with decreasing step size, confirming our speculation of an infinitesimal limit cycle. Finite oscillations are never observed in our numerical study with numerous parameter values. The frequency dependence on N_3 and θ reported in the paper must then be considered meaningless.

CONCLUSION

We have demonstrated that the finite oscillations produced by the Vayenas *et al.* model are invalid. Modification of the present model is necessary before observable limit cycles can be simulated.

Another point that merits mentioning is the fact that according to an apparent inference of the Vayenas *et al.* model, even when N_3 is larger than $1/K^*$, violating condition C1, oscillations can still occur if the initial conditions are chosen such that they lie to the left of the stability surface (different from the side on which the steady states are located). This is never verified experimentally, even though such experiments seem easy to carry out. Moreover, since these conditions satisfy inequality (7), finite oscillations can never occur and the system is actually "stuck" to the stability surface at large time in an infinitesimal limit cycle if it starts from the appropriate side. Since this kind of limit cycle resembles steady states, the system should have, in effect, two steady states depending on the initial conditions (which side it starts from). This is verified in our numerical studies. However, such a phenomenon of steady-state multiplicity is also never observed experimentally, casting further doubt on the validity of the model.

REFERENCES

1. Vayenas C. G., Georgakis, C., Michaels J., and Tormo J., *J. Catal.* **67,** 348 (1981).
2. Vayenas C. G., Lee B., and Michaels J., *J. Catal.* **66,** 36 (1980).

HSUEH-CHIA CHANG
MOBOLAJI ALUKO

Department of Chemical and Nuclear Engineering
University of California
Santa Barbara, California 93106

Received July 24, 1981; revised September 3, 1981