JOURNAL OF CATALYSIS 90, 371–373 (1984)

LETTERS TO THE EDITORS

Comment on the "Interpretation of the Electromotive Forces of Solid Electrolyte Concentration Cells during CO Oxidation on Platinum" and on "Electromotive Forces Studies of CO Oxidation on Platinum"

In two recent papers Okamoto *et al.* (*1*, *2*) discuss experimental results obtained during CO oxidation on Pt catalyst films deposited on stabilized zirconia solid electrolyte and attempt to correlate the emf of the cell $O_2,CO,CO_2,Pt|ZrO_2(Y_2O_3)|Pt,O_2$ with the mechanism of CO oxidation on platinum. Although the papers contain some potentially interesting experimental information, the proposed interpretation of the kinetic and emf data (*2*) is quite questionable, sometimes self-conflicting, and apparently in violation of basic electrochemical principles.

The kinetic and emf data presented in Refs. (*1*, *2*) are puzzling since apparently no analysis was performed in the cell-reactor effluent and no information is given about the nature (e.g., differential) of the cell reactor. As a result, the actual meaning of P_{CO} and P_{O_2} used in all the experimental correlations is ambiguous, since the authors do not specify if these quantities refer to reactor inlet or effluent conditions. One cannot assume that the reactor was differential, since reactor conversion was never measured. Therefore the actual composition of the gas mixture exposed to the Pt catalyst–electrode is not known and may differ substantially from inlet conditions. As a result the experimental correlation of emf with P_{CO} and P_{O_2} becomes quite dubious, as the latter quantities are essentially unknown.

The discussion of the kinetic results is further obscured by the inappropriate use of the terms activation energy and Arrhenius plot (e.g., Figs. (5) and (11) of Ref. (*1*), which are clearly not Arrhenius plots).

However, more serious problems exist with the attempted interpretation of the emf data (*1*) and the resulting model (*2*). The authors provide no experimental justification for their claim that the emf corresponds to mixed potentials. Actually this claim is contradicted by Fig. 10 of Ref. (*2*) which shows that in region I the coverage of CO is practically zero.

Okamoto *et al.* base their argument for mixed potentials on the statement (*1*) that if E in region I reflects the activity a_0 of chemisorbed oxygen, then it is difficult to explain why a_0 in region I can be reduced by three orders of magnitude when small amounts of CO are added to the gas phase. They also cite UHV results (*3*) which show that addition of comparable amounts of CO reduces the oxygen coverage by only 50%. The entire argument is based on a confusion between oxygen coverage and oxygen activity. It is not realized in Ref. (*1*) that, according to any chemisorption isotherm, e.g., a Langmuir isotherm, activity can decrease by many orders of magnitude with less than 1% decrease in coverage, if one is near or on the flat (saturation) part of the isotherm. This is the case for oxygen on Pt in region I, as shown by the same authors (e.g., Fig. 10 of Ref. (*2*)). As an example, the similar behavior of cell emf with increasing fuel concentration during C_2H_4 oxidation on Pt has been adequately described by a simple Langmuir isotherm for atomic oxygen chemisorption (*4*).

In the fuel-rich region (III), when the cell emf exceeds 700 mV (*1*, *2*) and the surface is essentially saturated with CO, it is quite likely (*5*) that the exchange reaction

0021-9517/84 $3.00

$$CO_\sigma + O^{2-} \rightleftarrows CO_2 + 2e^- \qquad (1)$$

can take place in parallel with the exchange reaction

$$O^{2-} \rightleftarrows O_\sigma + 2e^- \qquad (2)$$

However, it is well established (*6*) that the concentration cell O_2,Pt|$ZrO_2(Y_2O_3)$|Pt,O_2 exhibits negligible anodic activation overpotential in comparison with the anodic overpotential of the cell CO,CO_2, Pt|$ZrO_2(Y_2O_3)$|Pt,O_2. This shows that the intrinsic exchange current density of reaction (1) is negligible compared with that of reaction (2), and therefore reaction (1) is likely to have no significant contribution to the emf even in region III, where CO coverage is nearly complete. Careful experimental investigation of the dependence of the anodic exchange current density on gaseous composition or preferably surface coverage during CO oxidation on Pt could quantify the extent to which reactions (1) and (2) contribute to the cell emf in region III. However, in region I where the surface coverage of CO is very small, reaction (1) can have only a negligible effect on the emf. It should be noted that previous solid electrolyte potentiometric (SEP) studies of catalytic oxidations (*4, 7*) were performed with cell emf's below 250 mV where the exchange reaction (2) clearly dominates.

The entire model presented in Ref. (*2*) to account for mixed potentials is based on Eq. (11) of Ref. (*2*). This equation, which assumes the net anodic half-cell reaction to be

$$CO_\sigma + O_\sigma \rightleftarrows CO_2 + 2\sigma \qquad (3)$$

is physically incorrect. Since E_m is defined in Ref. (*2*) as the "mixed electrode potential relative to the potential in the absence of CO," Eq. (11) implies that in the absence of CO (i.e., when $E_m = 0$ and $N_{CO} = 0$) the surface concentration of oxygen N_0 is zero, which is, of course, meaningless. Equation (10) of Ref. (*2*), from which Eq. (11) is derived, is also incorrect since according to the classical Butler–Volmer approach to electrode kinetics, e.g., see Ref. (*8*), the term E_m which appears in the equation should be the potential difference $\Delta\varphi$ between the electrode and the electrolyte and not the "mixed electrode potential relative to the potential in the absence of CO" (*2*). The same applies to Eqs. (22), (23), and (24) of Ref. (*2*) which account for "molecularly" chemisorbed oxygen. It follows therefore that the entire analysis and attempted correlation with experimental results in Ref. (*2*) is not meaningful.

One interesting result shown in Fig. 3 of Ref. (*2*) is that emf oscillations at 568 K start above roughly 150 mV, which is similar to what was observed during C_2H_4 oxidation on Pt (*4*). If reaction (2) is taken to be the exchange current reaction, then the emf value of 150 mV corresponds to a surface oxygen activity of 10^{-3} bar$^{1/2}$, i.e., $a_0 = (0.21)^{1/2} \exp(2FE/RT)$ bar$^{1/2}$ (*4*), where E (-150 mV) is the catalyst electrode potential minus the potential of the reference air electrode ($P_{O_2} = 0.21$ bar). This is within experimental error from the surface oxide stability limit at this temperature, which is calculated to be 2×10^{-3} bar$^{1/2}$ according to the direct high-temperature measurements of Berry (*9*) ($a_0^* = 2.4 \times 10^5 \exp(-10{,}550/T)$) and 0.2×10^{-3} bar$^{1/2}$ according to the emf data during ethylene oxidation on Pt (*4, 10*) ($a_0^* = 2.7 \times 10^5 \exp(-12{,}000/T)$) (*11*). This strongly suggests that rate and emf oscillations during CO oxidation on Pt can be caused by the same surface oxidation–reduction mechanism which has been used to describe semiquantitatively the limit cycle phenomena during C_2H_4 oxidation on Pt (*9*).

In summary the kinetic and emf data presented in Refs. (*1, 2*) are obscured by the lack of product analysis during the experiments. Furthermore, the attempted interpretation of the data is based on a physically incorrect equation.

REFERENCES

1. Okamoto, H., Kawamura, G., and Kudo, T., *J. Catal.* **82,** 322 (1983).

2. Okamoto, H., Kawamura, G., and Kudo, T., *J. Catal.* **82,** 332 (1983).
3. Matsushima, T., *Bull. Chem. Soc. Jpn.* **51,** 1956 (1978).
4. Vayenas, C. G., Lee, B., and Michaels, J. N., *J. Catal.* **66,** 36 (1980).
5. Fleming, W. J., *J. Electrochem. Soc.* **124,** 21 (1977).
6. Etsel, T. H., and Flengas, S. N., *J. Electrochem. Soc.* **118,** 1890 (1971).
7. Stoukides, M., and Vayenas, C. G., *J. Catal.* **82,** 45 (1983).
8. Wang, D. Y., and Nowick, A. S., *J. Electrochem. Soc.* **126,** 1155 (1979).
9. Berry, R. J., *Surf. Sci.* **76,** 415 (1978).
10. Vayenas, C. G., Georgakis, C., Michaels, J. N., and Tormo, J., *J. Catal.* **67,** 348 (1981).
11. Vayenas, C. G., and Michaels, J. N., *Surf. Sci.* **120,** L405 (1982).

C. G. VAYENAS

Department of Chemical Engineering
University of Patras
Patras
Greece

Received March 6, 1984