

Reply to the Letter to the Editor by J. Happel, "Kinetic Studies on the Mechanism of Catalytic Ethene Oxidation"

The differences between the versions of the Horiuti concept as developed by Temkin and by Happel and Sellers have been discussed by the latter authors (1), who criticized Temkin's use of "empty routes." In the present case, however, three mathematically independent routes result for the indicated sets of elementary steps P⁽¹⁾, P⁽²⁾, and P⁽³⁾, in agreement with Eq. 3 (2). Essentially, both procedures (2, 3) using the same elementary steps lead to two mechanisms: *m*₂, i.e., formation of ethene oxide (EO), corresponding to route P⁽¹⁾, as well as CO₂ + H₂O (P⁽²⁾) via a common surface complex consisting of adsorbed ethene at a site with adsorbed atomic oxygen, and *m*₃, i.e., formation of EO as in *m*₂ and CO₂ + H₂O (P⁽³⁾) via a different surface complex consisting of adsorbed oxygen at a site with adsorbed ethene.

The choice of elementary steps has been based on experimental findings (see Section IV in Ref. (2)), e.g., the common primary surface intermediate for P⁽¹⁾ and P⁽²⁾ (item iv), the second route P⁽³⁾ for total oxidation (item v), and the desorption of ethene (item ix). Therefore, it would appear obvious to start from the beginning with a combination of *m*₂ and *m*₃. In fact, it turns out that the separate use of either of the direct mechanisms is not in agreement with the experiments (see Fig. 11 in Ref. (2)). For *m*₂ (P⁽¹⁾ + P⁽²⁾) without P⁽³⁾) a constant *S*_{EO} would result, independent of *p*_E and *p*_{O₂}:

$$\frac{1}{S_{EO}} = 1 + \frac{k_5}{k_4} \quad (1)$$

and for *m*₃ (P⁽¹⁾ + P⁽³⁾) without P⁽²⁾):

$$\frac{1}{S_{EO}} = 1 + \frac{k_8}{k_1} \frac{p_E}{p_{O_2}} \frac{(k_9/k_{-8})p_{O_2}}{1 + (k_9/k_{-8})p_{O_2}} \quad (2)$$

leading to a constant intercept of 1.

The symbol "x" represents the P⁽³⁾ fraction of the total CO₂ + H₂O production according to P⁽²⁾ + P⁽³⁾. The values of x as a function of the experimental conditions (temperature, total pressure, *p*_E^o/*p*_{O₂}^o) can be obtained from the selectivity data. From the expressions for *r*₅ and *r*₉ in Eq. 17 (2) follows that

$$x = \frac{1}{1 + r_5/r_9} \quad (3)$$

where *r*₅/*r*₉ is obtained from Eqs. (12), (19a), and (19b) (2):

$$\frac{r_5}{r_9} = \frac{k_5/k_4}{1/S_{EO} - (1 + k_5/k_4)} \quad (4)$$

The dependence of the fraction x on *p*_E^o/*p*_{O₂}^o is illustrated in Fig. 1. For experiments with the same *p*_E^o the experimental values (■, □) are well described by the calculated curve (1), whereas for the same *p*_{O₂}^o, the calcu-

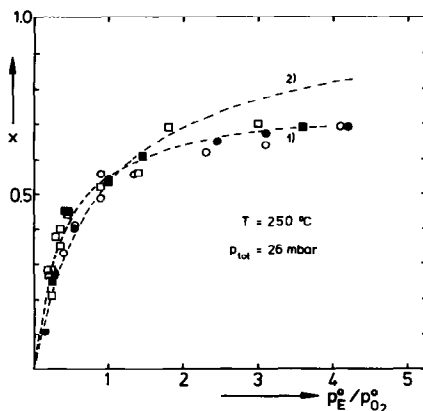


FIG. 1. Relative fraction of the route P⁽³⁾ of the total oxidation P⁽²⁾ + P⁽³⁾ vs educt ratio *p*_E^o/*p*_{O₂}^o. ■, Flow; □, batch experiments at *p*_E^o = constant 5.1 mbar; ●, flow; ○, batch experiments at *p*_{O₂}^o = constant 4.5 mbar. Broken lines calculated with Eqs. 3 and 4 and with Eq. 12 in Ref. (2): (1) for *p*_E^o = constant; (2) for *p*_{O₂}^o = constant.

lated curve (2) deviates from the experimental data (●,○) at $p_E/p_{O_2} > 1.5$. This deviation may be attributed to the saturation of the catalyst surface with adsorbed ethene at $p_E \cong 6$ mbar (see Sections V,3 and VI in Ref. (2)).

The above discussion and results show that the relative extent of the simultaneously proceeding mechanisms can well be computed from the experimental data by means of the procedure used in this case. On the other hand, it is not possible to model any selectivity obtained experimentally by either mechanism m_2 or m_3 as maintained by Happel (3). We are, of course, well aware that the trustworthiness of such evaluations of kinetic data rests on the choice of the elementary reaction steps. These have been selected on the basis of the presently available experimental findings. Further progress in the elucidation of the reaction mechanism can thus be

achieved only by a combination of kinetic studies with more detailed spectroscopic information on the nature of the intermediates under reaction conditions using well-defined catalysts.

REFERENCES

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