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V. Ravikumar^a; B. D. Kulkarni^a; L. K. Doraiswamy^a

^a National Chemical Laboratory, Pune, India

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INFLUENCE OF CATALYST DEACTIVATION ON THE NATURE OF THE STEADY STATE SOLUTIONS FOR REACTIONS ON CATALYTIC SURFACES†

V. RAVI KUMAR, B.D. KULKARNI and L.K. DORAISWAMY

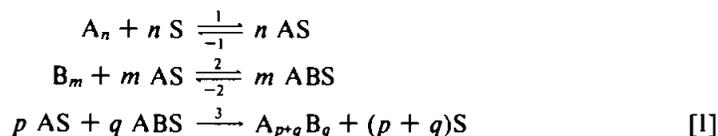
*National Chemical Laboratory
Pune 411 008, India*

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INTRODUCTION

Multistep catalytic reactions are known to exhibit multiplicity behaviour even in the absence of heat and mass transfer effects. Clearly, this is attributable to kinetic reasons, and a number of recent studies (Belyaev *et al.*, 1973; Sheintuch and Schmitz, 1977; Eigenberger, 1978; Ivanov *et al.*, 1980; Pikios and Luss, 1977) have analyzed the multiplicity and stability behaviour of different reaction mechanisms. In all these studies the underlying assumption has been that the total number of active centers on the surface of the catalyst remains unchanged during the progress of the reaction. In the event, however, when the reaction is accompanied by a loss of a certain number of sites, due to irreversible adsorption of impurities present in the feed stream or adsorption of the reactant itself, then the assumption of constant number of sites on the surface of catalyst is difficult to justify.

In the present investigation we consider the reaction mechanism in which reactant A_n forms a surface complex AS , reactant B_m reacts with this complex to give another complex ABS , and the two complexes react with each other to give the final product. It may be represented as



We shall analyze the consequences of this mechanism in the presence of effects that lead to a loss in the number of active centers. In the event when the rate of catalyst deactivation (or rate of loss of active centers) is sufficiently small in comparison with the rates of the other processes, the problem essentially reduces to one of obtaining first the behaviour of the system ignoring catalyst deactivation (i.e. at constant number

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of active centers) and then investigating change in the total number of sites with the progress of reaction (time). It is this case of slow deactivation that is considered here.

The reaction Scheme I with appropriate values of the parameters ($n = 2$, $m = 1$, $p = 1$, $q = 2$) represents the case of oxidation of ammonia, (Il'chenko *et al.*, 1974; 1975) and is interesting in that both the impact (step 2) and the interaction (step 3) mechanisms are simultaneously operative. Besides, the reaction involves a competitive-parallel reaction network with respect to the intermediates AS and ABS.

THEORY

The conservation equations with respect to the intermediate species can be written as:

$$\frac{d(\text{AS})}{dt} = k_1 p_A (S)^n - k_{-1} (\text{AS})^n - k_2 p_B (\text{AS})^m + k_{-2} (\text{ABS})^m - k_3 (\text{AS})^p (\text{ABS})^q \quad (1)$$

$$\frac{d(\text{ABS})}{dt} = k_2 p_B (\text{AS})^m - k_{-2} (\text{ABS})^m - k_3 (\text{AS})^p (\text{ABS})^q \quad (2)$$

Also at any instant of time the following equation representing conservation of active centers should hold:

$$L(t) = (S) + (\text{AS}) + (\text{ABS}) \quad (3)$$

Equations (1)–(2) can be expressed in dimensionless form in terms of surface coverages x and y of the two intermediate species:

$$\frac{dx}{d\theta} = a_1 (1 - x - y)^n - a_2 x^n - a_3 x^m + a_4 y^m - x^p y^q \quad (4)$$

$$\frac{dy}{d\theta} = a_3 x^m - a_4 y^m - x^p y^q \quad (5)$$

where the parameters a_1 – a_4 are defined as follows:

$$\begin{aligned} a_1 &= \frac{k_1 p_A}{k_3} L^{n-p-q} & a_3 &= \frac{k_2 p_B}{k_3} L^{m-p-q} \\ a_2 &= \frac{k_{-1}}{k_3} L^{n-p-q} & a_4 &= \frac{k_{-2}}{k_3} L^{m-p-q} \\ \theta &= k_3 L^{p+q-1} t & x &= \frac{(\text{AS})}{L}, \quad y = \frac{(\text{ABS})}{L} \end{aligned} \quad (6)$$

It is interesting to note that the parameters a_1 – a_4 depend on the total number of centers present at any instant and therefore vary with the progress of reaction. However, in view of the slower deactivation process considered, the rate of their change is sufficiently slow to justify the assumption of constancy for that instant.

RESULTS AND DISCUSSION

The steady state solutions to Eqs. (4) and (5) have been obtained for the specific case of $n = 2, m = 1, p = 1$ and $q = 2$. These stoichiometric coefficients typically correspond to the case of ammonia oxidation. No experimental data to precisely estimate the parameters (a_1-a_4) is available. However for real catalytic reactions the parameters normally lie within the range of (0-2). The parameters are thus arbitrarily chosen within this range for purpose of elucidation. For the values of the rate parameters used (a_1-a_4) only a unique steady state exists, and the stability of the steady state solution obtained using the linear stability analysis indicates that it is a stable solution. As a result of loss of active centres this steady state solution would alter, and several steady state solutions are generated corresponding to different values of L (and hence of the parameters a_1-a_4). For each of the solutions the linear stability analysis was carried out to check the stability. The steady state values of x and y are presented in Figure 1 for the corresponding value of L . The nature of the steady state solution is always stable for this case.

For ease of comparison and to help generalize the influence of loss of active centers

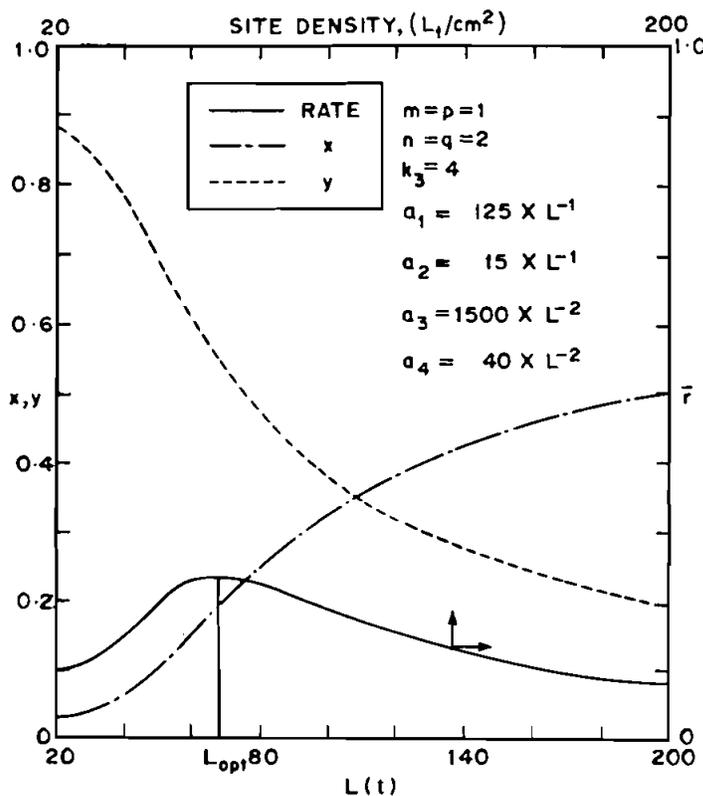
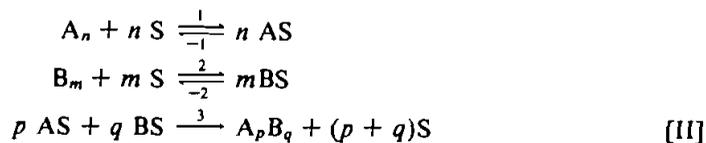


FIGURE 1 Dimensionless concentration of adsorbed intermediates and reaction rate per site (\bar{r}) as a function of total number of active centers (Mechanism I).

on the nature of the steady state solutions, solutions have also been obtained for another reaction mechanism:



Two subcases are analyzed for this reaction mechanism. In one it is assumed that the reaction occurs on a homogeneous surface, while in the other surface heterogeneity is accounted for through the variation of activation energy with surface coverage of one of the components (say [BS]) in a manner similar to that treated by Pikios and Luss (1977). The rate constant for the third step in the latter case is thus taken as:

$$k_3 = k_3^0 \exp\left(-\frac{E_3^0 + \alpha y}{RT}\right) \quad (7)$$

where E_3^0 is the activation energy when $y = 0$ and α is the coefficient of surface heterogeneity. The results for these two cases (also presented as x and y against the corresponding value of L) are shown in Figures 2 and 3. The nature of the steady state so-

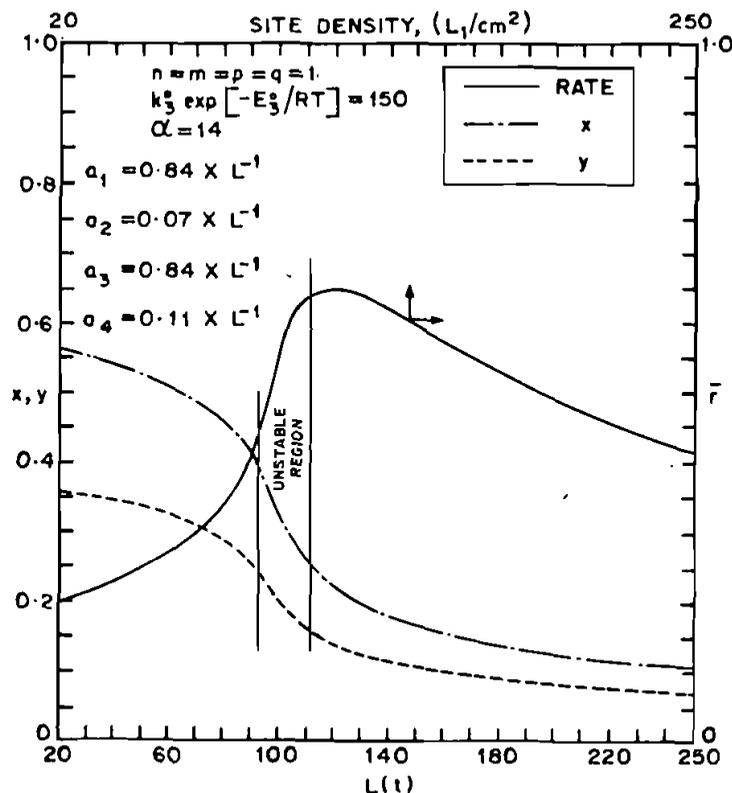


FIGURE 2 Dimensionless concentration of absorbed intermediates and reaction rate per site (r) as a function of total number of active centers (Mechanism II with surface heterogeneity taken into account).

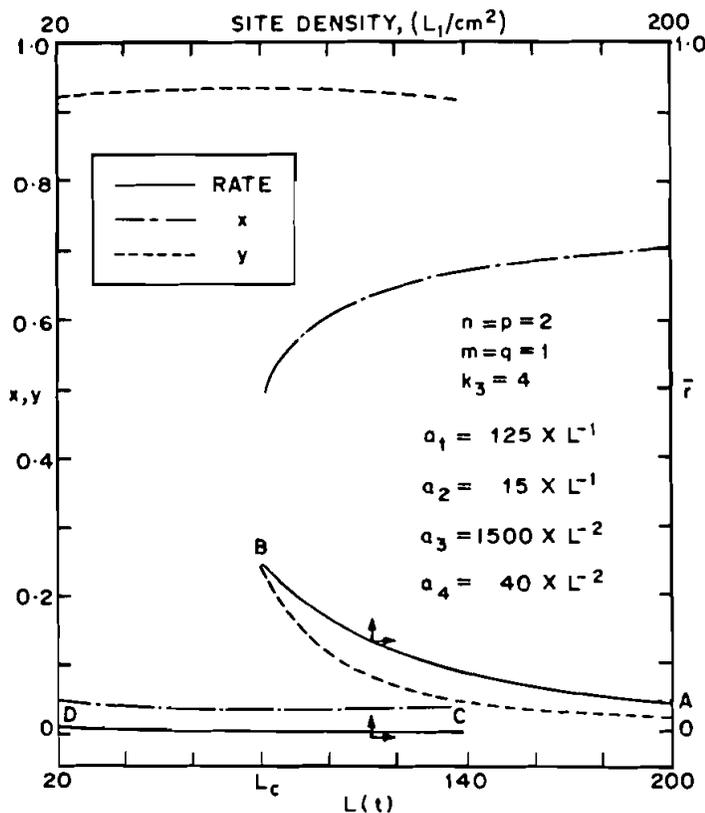


FIGURE 3 Dimensionless concentration of adsorbed intermediates and reaction rate per site (\bar{r}) as a function of total number of active centers (Mechanism II).

lutions [using linear stability analysis] when unstable is also indicated on the respective curves in Figure 2. In Figure 3 the nature of steady state solutions are, however, always stable.

Of greater importance than the coverage of species A and B with respect to L is the variation of the reaction rate. For mechanism I and II [step III] this can be written as

$$r = k_3 L^{p+q} x^p y^q \tag{8}$$

with the rate constant appropriately defined for each case. A plot of r vs L is dominated by the value of L^{p+q} and shows a monotonical increase of r with L . In most cases the coverages x and y tend to level off, thus masking any possible maximum in the rate.

It would be instructive to redefine the rate as

$$\bar{r} = \frac{r}{L^{p+q}} = k_3 x^p y^q \tag{9}$$

and plot it as a function of L site density (L_1/cm^2) as shown in Figures 1 to 4. The plots shown in these figures can be explained as follows.

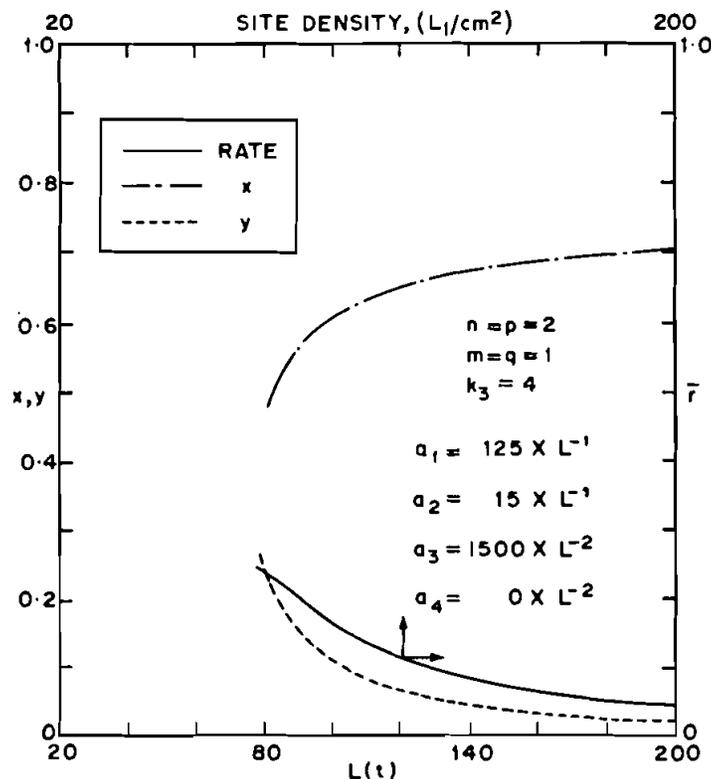


FIGURE 4 Dimensionless concentration of adsorbed intermediates and reaction rate per site (\bar{r}) as a function of total number of active centers (Mechanism II with step 2 irreversible).

On a surface of unit area with ($L = L_1$) number of sites (site density L_1/cm^2) this rate $\bar{r}(=r/L^{p+q})$ can be interpreted as the rate one would obtain if all sites except one are frozen. The variation of \bar{r} with L_1 in Figures 1-4 indicates that such a rate is a function of the environment (site density) and only for a specific site density, one can expect a maximum of \bar{r} . The rate \bar{r} [based on rhs of Eq. (9)] can also be interpreted as the extent of interaction among the adsorbed species leading to product formation on a site and hence a measure of its activity. The plot of \bar{r} vs L_1 therefore indicates the variation of activity of the site in relation to the packing site density on the surface. An optimum site density is seen to exist for each of the cases shown in Figures 1-4 and for a uniform distribution of sites on the surface, this corresponds to an optimum separation of sites. The conclusion of highest activity being realized for a specified separation of sites is known for certain specific cases [see Froment and Bischoff (1979)] and is generally proved here for the most common mechanisms.

Besides the important result of the activity exhibiting a maximum, the decay of the catalyst or more specifically the loss of active centers also aduces certain other features to the system depending on the reaction mechanism. For example, as evidenced in Figure 2, the nature of the steady state solution changes from unique stable steady state to unique unstable state that eventually changes back to stable steady state on further loss of sites. In the unique unstable region Pikios and Luss (1977) have pre-

dicted limit cycle behaviour. A qualitative change in the phase plane plot is therefore possible.

Figure 3 shows another interesting feature where, for the parameters values studied, multiplicity of steady states is indicated within a certain range of L values. Only the two stable solutions are shown in the figure, and it is seen that on reducing L the dimensionless rate follows the curve AB. At $L = L_c$ there is a sudden drop in the rate and on further loss of sites the rate moves along the curve CD. An interesting variation of this case is shown in Figure 4 where at $L = L_c$ the rate drops to zero. The specific case assumes the second step in the reaction mechanism II to be irreversible. For this case it can be easily shown that one of the steady states always corresponds to $x = 0$, $y = 1$ where the rate has a zero value. At $L = L_c$ the rate therefore jumps from one steady state solution to the other where no reaction can proceed. As a consequence, even when as many as L_c centers are still left on the surface, the reaction is extinguished. Clearly this is possible only if the second step is irreversible. For even a small value of the reverse rate constant the picture shown in Figure 3 holds.

CONCLUSIONS

To sum up, the present paper analyzes the most common types of reaction mechanisms to illustrate the influence of loss of active centers on the nature of steady state solutions. Using suitable examples it is shown that

- (1) the loss of active centers might induce a qualitative change in the phase plane plot,
- (2) there can exist a minimum value of the number of active centers on the surface below which no reaction can progress, and
- (3) there exists an optimum site density on the surface of the catalyst that would lead to largest interactions among the surface adsorbed species.

NOTATION

A, B	= reactant and product species
AS, BS, ABS	= adsorbed species
a_1, a_2, a_3, a_4	= parameters defined in Eq. 6
E_3^0	= activation energy for the third step when $y = 0$
$k_1, k_{-1}, k_2, k_{-2}, k_3$	= rate constants of mechanistic steps
k_3^0	= Arrhenius parameter for the third reaction step
L	= total number of active sites
L_1	= site density on the surface
n, m, p, q	= stoichiometric coefficients
p_A, p_B	= partial pressure of reactant species

r	= reaction rate defined in Eq. (8)
\bar{r}	= modified reaction rate defined in Eq. (9)
S	= active site
t	= time parameter
x, y	= dimensionless concentration of adsorbed species

Greek letters

θ	= dimensionless time
α	= coefficient of surface heterogeneity

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