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On the Kinetics of Self-Poisoning Catalytic Reactions

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The kinetics of self-poisoning reactions have been often described by empirical relations. Little attention has been given in the literature to the analysis of self-poisoning kinetics in relation to a reaction mechanism. In this paper the standard treatment of catalytic reactions is applied to reaction systems undergoing deactivation. It is shown that the kinetics of currently accepted poisoning models can be obtained using this treatment. Furthermore, it is shown that knowing the order of the poisoning kinetics on the active surface area will indicate the number of sites involved in the formation of surface residues. The approach presented here offers more insight into the basic processes occurring during self-poisoning than can be obtained from empirical rate laws.

NOMENCLATURE

A	reactant
[A·S]	adsorbed reactant
B	product
[B·S]	adsorbed product
C_A	reactant concentration, mol/cm^3
C_B	product concentration, mol/cm^3
k_i, k_{-i}	rate constants of i step
K_i	equilibrium constant for the i step
P_{H_2}	hydrogen partial pressure
R	steady state reaction rate, molecules/cm^2 sec
R_p	rate of poisoning, N^0 sites/cm^2/sec
S	empty active site
t	time, sec
X_0	initial site concentration, N^0 sites/cm^2
X_1	concentration of empty active sites, N^0 sites/cm^2
X_2	concentration of sites occupied by the adsorbed reactant, N^0 sites/cm^2
X_3	concentration of sites occupied by the adsorbed product, N^0 sites/cm^2
X_4	concentration of sites occupied by the poison N^0 sites/cm^2
W	poison species
θ	fraction of the initial sites which are unpoisoned, fractional surface

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INTRODUCTION

Catalyst poisoning is an important factor which in many cases determines the operation of catalytic reactors. Despite its importance, surprisingly little attention in the literature has been given to the analysis of the poisoning kinetics and its relation to the mechanisms of the poisoning. In most cases empirical methods have been used to correlate catalyst activity with reactor operating conditions. The object of this paper is to show that the standard treatment of catalytic reactions can be applied to deactivating systems to obtain poisoning rate laws identical in form to many of the currently accepted empirical

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poisoning laws. It is believed that this approach offers advantages over empirical methods in that it permits insights into the basic processes occurring.

Deactivation is a general designation and refers to processes that lower the catalyst activity. Herein deactivation processes which result from the association of species with the active sites that are not in the main sequence of the elementary steps are designated as poisoning. Deactivation processes which arise from sintering will not be treated.

Poisoning reactions can be further divided into two types:

i. Impurity poisoning, as the name implies, involves a poison precursor which enters as an impurity in the feed. Under reaction conditions the impurity reversibly, or irreversibly, adsorbs or reacts onto the active sites (*1*, *2*) removing them from use by species involved in the main reaction sequence.

ii. Self-poisoning: the poison precursor is the reactant or product. A short review of published work on self-poisoning mechanisms is presented below.

In the early studies of catalyst poisoning carried out by Voorhies (*3*) the amount of carbon on the surface was measured as a function of time on stream. Knowing the relation between conversion and carbon yield it was possible to obtain an empirical correlation between the conversion and process time. Eberly *et al.* (*4*) showed that Voorhies correlation was not unique but was a function of feed composition, reaction conditions, and feed rate. Following Voorhies' work, a number of studies were published wherein catalyst activity was studied in terms of carbon formation (*5–7*).

Furthermore, mechanisms describing the rate of carbon formation were proposed (*7*, *8*). Froment and Bischoff (*9*) realized that self-poisoning is caused by either reactant or product; therefore, the rate of carbon formation has to be in general a function of reactant or product concentration. The authors proposed that poisoning can be caused by reactions parallel or consecutive to the main reaction. However, Froment and Bischoff assumed, arbitrarily, that the preexponential terms of the poisoning rate were exponential or hyperbolic functions of the carbon content. Other authors (*10*, *11*) have used linear functions for the preexponential terms. Chieh (*12*) extended the series mechanism to Langmuir–Hinshelwood poisoning kinetics. Hegedus and Petersen (*13*) extended the series and parallel mechanism to include both series and parallel mechanisms occurring simultaneously, but at different rates. A summary of the poisoning kinetics was presented by Levenspiel (*14*) where it was shown that most of the empirical correlations proposed previously are particular cases of the parallel and series schemes.

Accordingly, parallel and series poisoning and their various combinations are useful models to study, and some of these forms are derived below using standard treatment of catalytic sequences.

Derivation of Poisoning Rate Expression from Catalytic Sequences

The following assumptions are made to derive the rate expression of catalytic sequences (*15*):

1. The total number of sites is constant.
2. The steady-state approximation is valid after an induction period.
3. There is a rate determining step in the reaction sequence.

When poisoning occurs the initial number of sites is not constant. However, it can be easily demonstrated that if there is a rate determining step in the main reaction sequence, and if that rate is much faster than the rate of poisoning which, of course, is almost always the case, then

the removal of active sites due to poisoning does not invalidate the steady-state assumption.

To derive the kinetics of a self-poisoning reaction, let us consider the case of parallel poisoning represented schematically by the following two reactions

$$\begin{aligned} A &\rightarrow B, \\ A &\rightarrow W, \end{aligned} \tag{1}$$

where A is the reactant, B the product, and w a surface residue. The above scheme can be represented alternatively by the following sequence of elementary steps

$$A + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [A \cdot S] \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} [B \cdot S] \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} B + S \tag{2}$$

$$[A \cdot S] \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} W$$

where S is an empty active site, [A·S] the adsorbed reactant, and [B·S] the adsorbed product. Further stipulations are necessary to make the sequence of steps of Eq. (2) match the parallel poisoning scheme of Eq. (1). In particular, certain restrictions are necessary as the relative magnitudes of the rate constants such as those given below.

$$k_{-2} \ll k_2 \ll k_1,\ k_{-1},\ k_3,\ k_{-3} \tag{3}$$

and

$$k_{-4} \ll k_4 < k_2. \tag{4}$$

If the initial surface concentration of sites is X_0 (N^0 sites/cm^2) then

$$X_1 + X_2 + X_3 + X_4 = X_0, \tag{5}$$

where X_1 is the surface concentration of empty active sites, S; X_2, X_3 and X_4 are the surface concentration of sites occupied by the adsorbed reactant [A·S], product [B·S], and poison, respectively.

Under the conditions given by Eqs. (3) and (4), the steady-state approximation can be applied for the empty site, adsorbed reactant and adsorbed product concentrations, hence the steady-state reaction rate is given by

$$R = k_2 X_2, \tag{6}$$

where R is the rate measured in molecules/cm^{2}sec, and the rate of poisoning is

$$R_p = \frac{dX_4}{dt} = k_4 X_2. \tag{7}$$

In accordance with Eq. (3), the concentrations X_2 and X_3 are related to X_1 by the equilibrium, relationships below:

$$X_2 = K_1 C_A X_1, \tag{8}$$

and

$$X_3 = K_3 C_B X_1. \tag{9}$$

Equations (8) and (9) are substituted into Eq. (5) to get

$$X_1 = \frac{(X_0 - X_4)}{(1 + K_1 C_A + K_2 C_B)}. \tag{10}$$

Equation (10) differs from the usual Langmuir–Hinshelwood result by the appearance of the term $X_0 - X_4$ in the numerator. The difference $X_0 - X_4$ corresponds to the unpoisoned sites in the system and appears in this form because the assumption has been made that the relaxation time for the main reaction to be approximated by the steady-state assumption is short compared to the time constant of the poisoning process. Accordingly, $X_0 - X_4$ replaces X_0 of the standard treatment to describe a deactivating process in a natural way.

If now the residual fraction of unpoisoned sites is defined as

$$\theta = \frac{X_0 - X_4}{X_0}, \tag{11}$$

then Eqs. (8), (10), (11), (6) and (7) lead to

$$R = \frac{X_0 k_2 K_1 \theta C_A}{(1 + K_1 C_A + K_2 C_B)}, \tag{12}$$

and

$$\frac{R_p}{X_0} = \frac{d\theta}{dt} = \frac{k_4K_1\theta C_A}{(1 + K_1C_A + K_2C_B)}, \quad (13)$$

which for the case of $1 \gg K_1C_A + K_2C_B$, i.e., at low surface coverages, yields

$$R = k_2X_0K_1\theta C_A, \quad (14)$$

$$-\frac{d\theta}{dt} = k_4K_1\theta C_A. \quad (15)$$

Equations (14) and (15) are similar to those proposed to describe parallel self-poisoning.

Consider now a different empirical scheme

$$\begin{matrix} A \to B, \\ B \to W, \end{matrix} \quad (16)$$

which is referred to as series self-poisoning. This can be represented alternately by the sequence of elementary steps given by Eq. (2) with the exception that the poison formation step should occur by

$$[B \cdot S] \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} W. \quad (16a)$$

A similar analysis to that used above leads to

$$R = k_2X_0K_1\theta C_A, \quad (17)$$

$$-\frac{d\theta}{dt} = k_4K_3\theta C_B. \quad (18)$$

Equations (17) and (18) are similar to those proposed to describe series self-poisoning.

Equations (14) and (15) are first order in both reactant concentration and θ. This dependence follows from the assumption that there is only one active site involved in the elementary step of the main reaction and the poisoning reaction, i.e.,

$$[A \cdot S] \overset{k_3}{\to} [B \cdot S], \quad (19)$$

$$[A \cdot S] \overset{k_4}{\to} W. \quad (20)$$

The same is true for the series poisoning case.

Consider next a more complex series of elementary steps for a parallel self-poisoning mechanism given below:

$$\begin{matrix} A + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [A \cdot S] \overset{k_2}{\to} [B \cdot S] \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} B + S, \\ k_4 \downarrow\uparrow k_{-4} \\ 2P + nH_2 \\ k_5 \downarrow \\ W \end{matrix} \quad (21)$$

where

$$k_2 \ll k_1,\ k_{-1},\ k_3,\ k_{-3},\ k_4,\ k_{-4}, \quad (22)$$

$$k_5 \ll k_2, \quad (23)$$

and where we assume that

$$\frac{dX_5}{dt} = k_5X_4^2. \quad (24)$$

The concentrations X_4 and X_5 correspond to surface concentrations of P and W, respectively.

Note also that details of how the n molecules of hydrogen are removed at the surface are not specified. However, these details are unimportant if the hydrogen is removed by a series of equilibrium steps.

An analysis of this system leads to

$$R = k_2X_0K_1C_A\theta, \quad (25)$$

$$\frac{dX_5}{dt} = \frac{k_5(X_0K_1K_4C_A)^2}{(P_{H_2})^n(1 + K_1C_A + K_2C_B)^2}, \quad (26)$$

or for small surface coverages.

$$-\frac{d\theta}{dt} = k_5X_0K_1^2K_4^2\frac{\theta^2C_A^2}{(P_{H_2})^n}, \quad (27)$$

which gives second order dependence of the rate of poisoning with θ.

Furthermore, θ does not appear in the denominator of the poisoning rate expressions, therefore, according to this model the order in θ indicates the number of sites involved in the poisoning mechanism.

It has been observed experimentally that the rate of poisoning occurring during

catalytic reforming decreases as the H_2 pressure is increased. The hydrogen pressure dependence of the poisoning rate is understandable in terms of the sequence of steps given by Eq. (21) and the appearance of the hydrogen partial pressure in the denominator of Eq. (27) in agreement experimental observation.

In conclusion, it is possible to use the steady-state approximation to analyze self-poisoning reactions in the same way as catalytic sequences are analyzed, provided that the time constant for poisoning is smaller than the time constant of the main reaction. Using this procedure various rate laws of poisoning can be derived based on a reaction mechanism. Conversely knowing the order of the poisoning reaction on the fractional activity θ, it is possible to infer the poisoning mechanism.

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