Catalyst Deactivation by Multilayer Coking: A Kinetic Model

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INTRODUCTION

The usual framework within which coking is analyzed is based on separable kinetics, in which the effect of deactivation is factored out. Thus, kinetic dependencies, which are time-independent, and activity dependencies, which are not, are separable (Butt, 1972). Separable kinetics in one form or another have been used extensively to describe coking behavior (Wojciechowski, 1968; Krishnaswamy and Kittrell, 1979). Szepe and Levenspiel (1970) proposed the use of power law expressions for separable kinetics. Application of separable kinetics to coking, however, poses a problem because of a feature that is unique to deactivation by coking, namely, "multilayer" formation of coke. Coke can be anything from pure carbon to hydrogen-deficient carbon compounds of high molecular weight, and thus the term "multilayer" cannot be defined rigorously. It is well known that typical coke content readily exceeds the amount corresponding to a monolayer coverage of catalyst (Butt, 1972). The fact that the coke content exceeds the "monolayer" coverage and yet the catalyst retains its residual activity implies the formation of many layers of coke. The multilayer formation could be due to the growth mechanism observed by Trimm (1976) and Baker and Waite (1975), or be due to simple deposition of coke precursor onto the coke already on the catalyst. Often, a linear relationship between deactivated area and coke content is assumed. This approach, however, completely neglects the multilayer nature of coking.

In this paper, we present a model that accounts for the multilayer nature of coking. The basic concept is not that coke grows in single polymer molecules, as in the model of Beeckman and Froment (1980), but rather that coke deposits on the catalyst surface in successive layers, with each layer covering a fraction of the one immediately below it, analogous in its concept to the BET theory (Brunauer et al., 1938). Rather than assuming that individual sites grow coke at a constant rate as in the Beeckman-Froment model (BF model), it is assumed that at any given time, the coke distribution can consist of any number of layers from one (monolayer) to N layers. The layer buildup is represented by a series of elementary surface reactions that lead directly to a relationship between coke content and the fraction of catalyst deactivated. Thus, the model views coking as a series of surface reactions involving mono- and multilayers of coke. In contrast, the BF model treats coking as a random process with certain probabilities assigned to the events of site coverage and the blocking by the deposited coke based on probability laws. The series of surface reactions and the corresponding kinetics lead directly to coking kinetics. Although only a finite number of layers should be involved, we will consider first the extreme case of an infinite number of layers, since it brings out the essential features of the multilayer model in a concise form.

A MULTILAYER MODEL

Consider a system in which both the main and coking reactions occur on the same sites. Suppose that all sites remain accessible to the reactants. Suppose further that coke precursor P can form coke upon deposition onto sites whether the sites are vacant or occupied by coke. The multilayer coking can then be represented by the following irreversible elementary surface reactions (adsorption steps):

$$P + S \xrightarrow{k_{p_c}} P{\cdot}S\downarrow \qquad \text{monolayer coking}$$

$$\left.\begin{array}{l} P + P{\cdot}S \xrightarrow{k_{p_1}} (2P){\cdot}S\downarrow \\ P + (2P){\cdot}S \xrightarrow{k_{p_2}} (3P){\cdot}S\downarrow \\ \quad\vdots \\ P + (nP){\cdot}S \xrightarrow{k_{p_n}} [(n+1)P]{\cdot}S\downarrow \end{array}\right\} \text{multilayer coking}$$

The first step is for monolayer coking, since one "molecule" of coke precursor adsorbs onto a vacant site S to form monolayer coke. Multilayer coke forms, as shown, when the precursor deposits onto a mono- or multilayer coke.

The net rates for the coking steps are

$$R_{p\cdot s} = k_{p_c}C_pC_v - k_{p_1}C_{p\cdot s}C_p \tag{1}$$

$$R_{2p\cdot s} = k_{p_1}C_{p\cdot s}C_p - k_{p_2}C_{2p\cdot s}C_p \tag{2}$$

$$R_{3p\cdot s} = k_{p_2}C_{2p\cdot s}C_p - k_{p_3}C_{3p\cdot s}C_p \tag{3}$$

$$\vdots$$

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$$R_{np\cdot s} = k_{p(n-1)}C_{(n-1)p\cdot s}C_p - k_{p_n}C_{np\cdot s}C_p \tag{4}$$

$$\vdots$$

where C_p is the concentration of coke precursor, C_v is the surface concentration of vacant sites, and $C_{np\cdot s} (n = 1, 2, \ldots, N)$ is the surface concentration of active sites occupied by mono ($n = 1$) and multilayer ($n > 1$) coke. N is the total number of coke layers. It should be noted that $C_{np\cdot s}$ is not the concentration of coke but the concentration of *sites* occupied by various kinds of coke. If we assume that the rate constants for the formation of all multilayer coke are the same, we have

$$k_{p_1} = k_{p_2} = \cdots = k_{p_n} = k_p \tag{5}$$

The assumption involves a hypothesis that the affinity of coke to precursor is the same regardless of the number of coke layers.

Consider the distribution of multilayer coke at any given time. In order to obtain the distribution, we seek a relationship between the site concentrations of multilayer coke in two successive multilayers, i.e., $C_{(n-1)p\cdot s}$ and $C_{np\cdot s}$. For this, we combine Eqs. 3 through 5 to obtain

$$\frac{R_{(n-1)p\cdot s}}{R_{np\cdot s}} = \frac{dC_{(n-1)p\cdot s}}{dC_{np\cdot s}} = \frac{C_{(n-2)p\cdot s} - C_{(n-1)p\cdot s}}{C_{(n-1)p\cdot s} - C_{np\cdot s}} \tag{6}$$

Note that Eq. 6 is satisfied if it is assumed each layer occupies a certain portion of the one below it:

$$\frac{C_{np\cdot s}}{C_{(n-1)p\cdot s}} = f \tag{7}$$

where f is a constant that describes the distribution of layers at any given time. To proceed further, we combine Eqs. 1 and 2 to obtain

$$\frac{R_{p\cdot s}}{R_{2p\cdot s}} = \frac{dC_{p\cdot s}}{dC_{2p\cdot s}} = \frac{K_pC_v - C_{p\cdot s}}{C_{p\cdot s} - C_{2p\cdot s}}; \quad K_p = k_{p_c}/k_p \tag{8}$$

If we assume that Eq. 7 holds for the relationship between monolayer and dilayer coke, we have

$$fC_{p\cdot s} = C_{2p\cdot s} \tag{9}$$

Combining Eqs. 8 and 9 yields

$$\frac{1}{f} = K_p\frac{C_v}{C_{p\cdot s}} \tag{10}$$

Thus, the distribution of vacant sites and the sites occupied by mono- and multilayer coke can be determined if a relationship between C_v and $C_{p\cdot s}$ is known. Further, the distribution factor f has to be known.

Consider site balances (e.g., Butt, 1980) for the determination of the distribution factor f. A balance for the total sites is

$$C_t = C_v + \sum_{n=1}^{N} C_{np\cdot s} + \sum_i C_{i\cdot s} \tag{11}$$

If we restrict our attention to the coking in which the main and the coking reactions occur on the same active sites, we have

$$C_t\gamma = \sum_{n=1}^{N} C_{np\cdot s} \tag{12}$$

where γ is the fraction of catalyst deactivated. Thus, we have from Eqs. 11 and 12

$$C_t(1-\gamma) = C_v + \sum_i C_{i\cdot s} \tag{13}$$

The concentrations of the surface intermediates can be expressed in terms of reactant and product concentrations and C_v, given the elementary steps of the main reaction. In general, the righthand side of Eq. 13 can be expressed (Butt, 1980) as

$$C_v + \sum_i C_{i\cdot s} = C_v\left[1 + \sum_i (K_iC_i)^{m_i}\right]^n \tag{14}$$

Combining Eqs. 13 and 14 yields

$$\frac{C_v}{C_{p\cdot s}} = \left(\frac{C_t}{C_{p\cdot s}}\right)\left[\frac{1-\gamma}{(1+G)^n}\right] \tag{15}$$

The fraction of catalyst deactivated, γ, can be related to the distribution factor f through Eqs. 7, 9, and 12:

$$C_t\gamma = C_{p\cdot s}\left[\frac{1-f^N}{1-f}\right] \tag{16}$$

provided f is less than unity. For the infinite number of layers being considered in this section, Eq. 16 reduces, after rearrangement, to

$$\frac{C_t}{C_{p\cdot s}} = \frac{1}{\gamma(1-f)} \quad f < 1 \tag{17}$$

Combining Eqs. 10, 15, and 17 yields

$$f = \frac{1}{1 + \bar{K}_p(1-\gamma)/\gamma}; \quad \bar{K}_p = \frac{K_p}{(1+G)^n} \tag{18}$$

Now that the distribution is known, the relationship between coke content and the fraction of catalyst deactivated can readily be obtained. If we let q be the monolayer coke weight per site, we have

$$\begin{aligned} C_c &= q\sum_{n=1}^{N} n\,C_{np\cdot s} \\ &= q\,C_{p\cdot s}\left[\frac{f(1-f^N) - Nf^N(1-f)}{(1-f)^2} + \frac{1-f^N}{1-f}\right] \end{aligned} \tag{19}$$

where C_c is the coke content in weight per unit surface area. Upon substituting Eq. 16 for $C_{p\cdot s}$ into 19, the following relationship between C_c and γ results:

$$\frac{C_c}{Q} = \gamma\left[\frac{1}{1-f} - \frac{Nf^N}{1-f^N}\right] \tag{20}$$

where Q ($= C_tq$) is the weight of coke required to cover all active sites with one coke layer. For the infinite layer being considered, the relationship reduces to

$$\frac{C_c}{Q} = \frac{\gamma}{1-f} \tag{21}$$

Equation 18 allows us to rewrite Eq. 21 as follows:

$$\frac{C_c}{Q} = \gamma\left[1 + \frac{\gamma}{\bar{K}_p(1-\gamma)}\right] \tag{22}$$

The coke content due to multilayer coke or coke growth is contained in the second term in the bracket of Eq. 22 since $C_c/Q = \gamma$ when only monolayer coke is involved. For strictly monolayer coking, $\bar{K}_p$ approaches infinity since then $k_p = 0$ and thus the result reduces to the monolayer coking. Because of the infinite number of layers being allowed, the coke content becomes infinite when $\gamma = 1$.

The residual catalytic activity remaining after deactivation, A, which is the ratio of the rate of the coked catalyst to the rate of fresh catalyst, is not necessarily equal to the fraction of vacant sites. For the system being considered, however, we may assume the following relationship:

$$A = 1 - \gamma \tag{23}$$

Then the fractional activity of catalyst is related to the coke content from Eq. 22 as follows:

$$\frac{C_c}{Q} = (1 - A)\left[1 + \frac{1 - A}{\overline{K}_p A}\right] \tag{24}$$

FINITE NUMBER OF LAYERS AND STEPWISE PROCEDURES

As indicated earlier, physical reasoning should dictate that there be a finite number of coke layers. For a finite number of layers, the relationship between coke content and the fraction of catalyst deactivated is given by Eq. 20 with the distribution factor f given by

$$\frac{1 - f}{f(1 - f^N)} = \frac{K_p(1 - \gamma)}{\gamma(1 + G)^n} = \frac{\overline{K}_p(1 - \gamma)}{\gamma} \tag{25}$$

which follows from Eqs. 10, 15, and 16. It should be recognized that the distribution factor for infinite N is essentially the same as that for finite N for relatively small values of γ. Thus, the results obtained in the previous section for infinite layers can describe the initial stage of coking when γ is relatively small. For this initial stage, Eq. 24 can be rewritten in the following linear form:

$$\frac{C_c}{1 - A} = Q + \left(\frac{Q}{\overline{K}_p}\right)\left(\frac{1 - A}{A}\right) \tag{26}$$

if we assume that $A = 1 - \gamma$.

Consider the stepwise procedures one can use when a finite number of layers must be dealt with. For illustration purposes, we use the data obtained by Dumez and Froment (1976), which are perhaps the only published data stated to be diffusion-free. The multilayer model results given in terms of residual activity are for diffusion-free reactions. Since their fractional activity vs. coke content data are for various concentrations of reactants, details of which are not given, the average activities at various coke contents are used in the illustration. The average activities are the center points of the vertical lines in Figure 1, which is a linear plot of Eq. 26. It was assumed for the plot that $A = 1 - \gamma$.

As indicated earlier, the infinite layer result should be applicable in the initial stage of deactivation when γ (or $(1 - A)$) is relatively small. It is seen from the figure that the infinite layer results of Eq. 26 is applicable up to $A = 0.45$ or up to $\gamma = 0.55$. Since both finite and infinite layer results are applicable in the initial stage, the slope and the intercept of the straight line in Figure 1 yield the monolayer coke content Q and the parameter $\overline{K}_p$, respectively, which are also valid for the finite layer result. The values determined from the straight line in Figure 1 are 0.015 g coke/g catalyst for Q and 0.96 for $\overline{K}_p$. The relationship predicted by the infinite layer result (Eq. 24) is shown by the line of dots in Figure 2. As expected, the infinite layer result predicts higher coke contents than the experimental coke contents at lower activities. It is apparent that the finite layer result is needed to describe the relationship over the entire range of activity of interest.

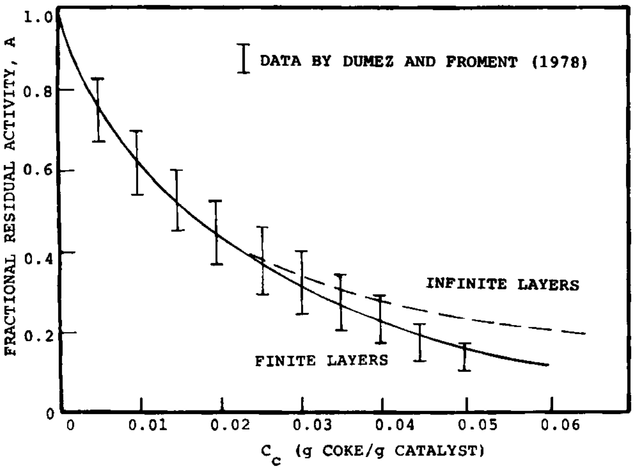

Figure 1. Determination of monolayer coverage and the rate constant ratio $\overline{K}_p$ from experimental data.

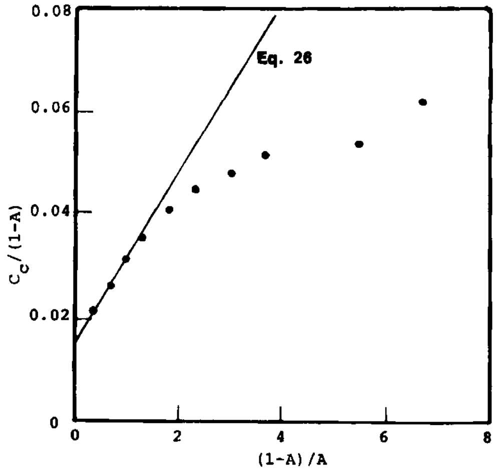

Figure 2. Comparison of catalytic activity determined by multilayer technique with experimental data.

The number of layers N has to be determined first to use the finite layer result. In the light of the discussion in the previous section regarding the effect of N on the distribution factor f, it is sufficient for the entire range of γ to determine N for the largest γ of interest since f increases with γ and thus the effect of N on γ (or f) and eventually on C_c is negligible for small γ. The value of N determined for the largest γ, therefore, will yield accurate results for the entire range of γ of interest. For the data being considered, the largest γ is that corresponding to $A = 0.12$ ($\gamma = 0.88$) for which $C_c = 0.06$ in Figure 2. Using the value of Q and $\overline{K}_p$ determined from Figure 1, the value of N can be determined from Eqs. 20 and 25, which for $Q = 0.015$ and $\overline{K}_p = 0.96$ are

$$C_c = 0.06 = 0.0132\left[\frac{1}{1 - f} - \frac{Nf^N}{1 - f^N}\right]$$

$$\frac{1 - f}{f(1 - f^N)} = \frac{0.96A}{1 - A}; \quad A = 0.12$$

The solutions obtained are $N = 8.4$ and $f = 0.98$. Now that N is determined, Eqs. 20 and 25 written in the following form can be used to describe the relationship between A and C_c for $\gamma > 0.55$ or $A < 0.45$:

$$C_c = 0.015\gamma\left[\frac{1}{1 - f} - \frac{8.4f^{8.4}}{1 - f^{8.4}}\right]$$

$$\frac{1 - f}{f(1 - f^{8.4})} = \frac{0.96A}{1 - A}$$

For a given A, the second equation is first solved for f, which, when used in the first equation, yields the coke content corresponding to that particular activity. The relationship thus obtained is shown in Figure 2 as the solid line. It is seen that the finite layer result describes quite well the relationship between A and C_c.

CONCLUSION

A physical model for multilayer coking has been developed for intrinsic kinetics based on surface coking reactions leading to the formation of multilayer coke. The model yields coke content in terms of fraction of catalyst deactivated (or residual activity when appropriate) and the parameters involving coke content corresponding to monolayer coverage, a measure of the rate of monolayer coke formation relative to that of multilayer coke formation, and the number of multilayers when the finite layer case is involved. These parameters can be determined in a straightforward manner from experimental values of residual activity and coke content. Independent experiments can be carried out to verify the parameter values for credence. For typical activity ranges of practical interest, the simple infinite layer result (Eq. 26) can be used. The concept and approach taken here can be utilized to describe various types of multilayer coking.

NOTATION

A = fractional catalytic activity remaining after deactivation
C_A, C_B = concentration of gaseous species A and B, respectively, mol/vol
C_c = coke content in weight coke/catalyst surface area, g/m^2
C_i = concentration of gaseous species i, mol/vol
C_p = concentration of coke precursor, mol/vol
C_t = total number of active sites/catalyst surface area, sites/m^2
C_v = number of vacant sites/catalyst surface area, sites/m^2
$C_{i\cdot s}$ = concentration of surface intermediate i, mol/vol
$C_{np\cdot s}$ = number of sites occupied by coke consisting of n (sites/m^2) layers/catalyst surface area
f = distribution factor given in Eq. 7
G = $\Sigma (K_i C_i)^{m_i}$
k = rate constant for main surface reaction
k_p = rate constant for multilayer coking reaction, vol · area/mol · time
k_{p_c} = rate constant for monolayer coking reaction, vol · area/mol · time
k_{p_n} = rate constant for multilayer coking reaction involving the coke of n layers, vol · area/mol · time
K_A, K_B = equilibrium constants for elementary reaction steps
K_i = equilibrium constant for the elementary step involving surface intermediate i
K_p = k_{p_c}/k_p
$\overline{K}_p$ = $K_p/(1 + G)^n$
m_i = constant in Eq. 15
n = subscript for number of coke layers; constant in Eq. 15
N = maximum number of coke layers
P = coke precursor
$P\cdot S$ = monolayer coke
$(nP)\cdot S$ = multilayer coke involving n layers of coke
q = weight of monolayer coke per site
Q = weight of coke when catalyst is covered by monolayer coke/catalyst surface area, $C_t q$, g/m^2
r_c = intrinsic rate of main reaction
R_p = rate at which the number of active sites changes, sites/time
$R_{np\cdot s}$ = net rate of reaction for the coke consisting of n layers, sites/time
S = active site
γ = fraction of catalyst deactivated

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