Catalyst Deactivation by Site Coverage through Multi-Site Reaction Mechanisms

IN-SIK NAM AND G. F. FROMENT

Laboratorium voor Petrochemische Techniek, Rijksuniversiteit Gent, Krijgslaan 281, B-9000 Gent, Belgium

Catalyst deactivation by site coverage is stochastically described for single- and dual-site reaction mechanisms for the main and the coking reactions of a catalytic process. Nonlinear relations between the deactivation function and the degree of site coverage are obtained for dual-site mechanisms. When the main and the coking reactions involve a different number of sites, the respective deactivation functions are not identical. When the coking reaction occurs on dual sites, the deactivation rate of the coking reaction depends on the number of sites in the cluster and therefore becomes structure sensitive, a feature that cannot be revealed by the classic phenomenological approach. © 1987 Academic Press, Inc.

INTRODUCTION

In many catalytic processes undesired side reactions lead to the deactivation of the catalyst by the formation of carbonaceous material, conveniently referred to as "coke." The deactivation decreases the rates of both the main and the coking reaction(s), but not necessarily in the same way. Froment (1) related the deactivation to the amount of deactivating agent and, within the framework of the kinetic formalism of Hougen and Watson, derived the following expressions for the deactivation functions for the main and coking reactions, respectively:

$$\varphi_A = \left(\frac{C_t - C_{Cl}}{C_t}\right)^{n_A} = (1 - \omega)^{n_A} \quad (1)$$

$$\varphi_C = \left(\frac{C_t - C_{Cl}}{C_t}\right)^{n_C} = (1 - \omega)^{n_C}. \quad (2)$$

These equations are based on the assumptions that the main and coking reactions occur on the same sites and that the deactivation is caused by site coverage only. The symbol C_{Cl} stands for the concentration of sites covered with coke precursor, i.e., the first component in the sequence ultimately yielding coke that is irreversibly adsorbed on the sites. This concentration has to be linked to the observable coke content of the catalyst.

As shown in Eqs. (1) and (2), it is clear that φ_A and φ_C are not identical when the number of sites involved in the main and coking reactions is not the same. The phenomenological approach described above assumes unlimited availability of sites for dual-site or multi-site formation. It does account for the decrease in total number of sites but not for the influence this may have on the possibility of dual (or multi) site formation.

In the present paper this influence is explicitly accounted for. To do so, the sites are assumed to be localized in clusters or ensembles. These are defined as a set of sites that are sufficiently close to one another to form the dual site required for the given reaction. This set of sites should not be confused with a cluster of metal atoms, e.g., the cluster of sites is assumed not to interact with neighboring clusters.

With the definition of cluster used here the availability of sites for dual-site formation is fully determined by the number of sites which are not covered yet. To account for this feature, a stochastic approach was

271

chosen, following the lines proposed by Beeckman and Froment (2) for single-site reactions. Four different cases were considered: in Case I, both the main and the coking reactions occur on a single site; in Case II, the main reaction occurs on dual sites and the coking reaction on a single site; in Case III, the main reaction occurs on a single site and the coking reaction on dual sites; in Case IV, both reactions occur on dual sites. First, the deactivation functions are developed for uniform clusters and later for clusters of unequal sizes.

METHODS AND RESULTS

Uniform Clusters

The main and coking reactions are assumed to occur on the same type of reaction sites. It is also assumed that the surface reaction is the rate-determining step in both the main and coking reactions.

The rate of coking is taken to be much lower than the rate of the main reaction. This implies that the momentary occupation of sites by the species involved in the main reaction does not affect the availability of these sites for the coking reaction.

The deactivation functions evidently depend on the reaction mechanisms, in particular on that of the coking. The reaction mechanisms are presented in Table 1. Two types of dual-site coking mechanisms are considered: Type 1, in which only one of the two sites involved remains covered with coke, and Type 2, in which both sites involved remain covered with coke. Sites participating in the main reaction are always regenerated.

Case I: Both Main and Coking Reactions on a Single Site (1–1 Reaction)

The deactivation functions and the degree of coverage for this case have been developed already by Beeckman and Froment (2a). For the sake of clarity, their definitions and results are briefly summarized here.

TABLE 1

Reaction Mechanisms

Case I. Main and coking reactions on single sites (1–1 reaction)
  (1) Main reaction:
$$A + \ l \rightleftarrows Al$$
$$Al \rightleftarrows Bl$$
$$Bl \rightleftarrows B + l$$
  (2) Coking reaction:
$$Al \ (\text{or} \ Bl) \rightarrow Cl$$

Case II. Main reaction on dual sites and coking reaction on single sites (2–1 reaction)
  (1) Main reaction:
$$\begin{array}{ll} A + \ l \rightleftarrows Al & \qquad A + \ l \rightleftarrows Al \\ Al + \ l \rightleftarrows Bl + l \quad \text{or} & \quad Al + \ l \rightleftarrows Bl_2 \\ \qquad Bl \rightleftarrows B + l & \qquad Bl_2 \rightleftarrows B + 2l \end{array}$$
  (2) Coking reaction:
$$Al \ (\text{or} \ Bl) \rightarrow Cl$$

Case III. Main reaction on single sites and coking reaction on dual sites (1–2) reaction
  (1) Main reaction: same as I(1)
  (2) Coking reaction:
$$\begin{array}{ll} \text{Type 1 coking} & \quad \text{Type 2 coking} \\ Al \ (\text{or} \ Bl) + l \rightarrow Cl + l & \quad Al \ (\text{or} \ Bl) + l \rightarrow Cl_2 \end{array}$$

Case IV. Main and coking reactions on dual sites (2–2 reaction)
  (1) Main reaction: same as II(1)
  (2) Coking reaction: same as III(2)

Let $S(t)$ be the probability that a site is active, i.e., not covered with coke at time t and coverage ω:

$$S(t) = \exp\left(-\int_0^t r_s^0 \, dt\right), \quad (3)$$

where $r_s^0 \, dt$ is the probability that a site is covered in the time interval dt. For a constant gas-phase composition, (3) reduces to

$$S(t) = \exp(-r_s^0 t). \quad (4)$$

For a 1–1 reaction, the deactivation functions are identical and defined by

$$\varphi_A = \varphi_C = \frac{\text{Total number of sites still active at coverage } \omega}{\text{Total number of sites at zero coverage}} \quad (5)$$

with

$$\omega = \frac{\text{Total number of sites covered with coke}}{\text{Total number of sites at zero coverage}}. \quad (6)$$

Suppose that all clusters on the catalyst surface contain an equal number of sites, n. Let $\sigma' A_S$ be the total number of sites on a catalyst particle, where σ' is the site density based on the catalyst surface area and A_S is the total catalyst surface area. The number of clusters containing n sites is

given by $\sigma' A_S/n$. Therefore, Eqs. (5) and (6) can be written, for a given gas phase composition, as

$$\varphi_A = \varphi_C = \frac{\sigma' A_S S}{\sigma' A_S} = S = \exp(-r_s^0 t) \quad (7)$$

$$\omega = \frac{\sigma' A_S - \sigma' A_S S}{\sigma' A_S} = 1 - S$$

$$= 1 - \exp(-r_s^0 t). \quad (8)$$

After substitution of Eq. (8) into Eq. (7), the deactivation functions can be written in terms of the degree of coverage:

$$\varphi_A = \varphi_C = 1 - \omega. \quad (9)$$

Both deactivation functions exhibit a nonlinear relation with respect to the reduced time, $r_s^0 t$, while they show a linear relation with respect to the degree of coverage. This is illustrated in Fig. 1.

Case II: Main Reaction on Dual Sites and Coking Reaction on a Single Site (2–1 Reaction)

The deactivation function for a dual-site reaction is still the probability that a site is active at coverage ω, but a distinction has to be made between active sites and sites that are not covered with coke, that is, free sites. The term "active" now implies that the site has a neighbor in the cluster which is free of coke and with which it can form a
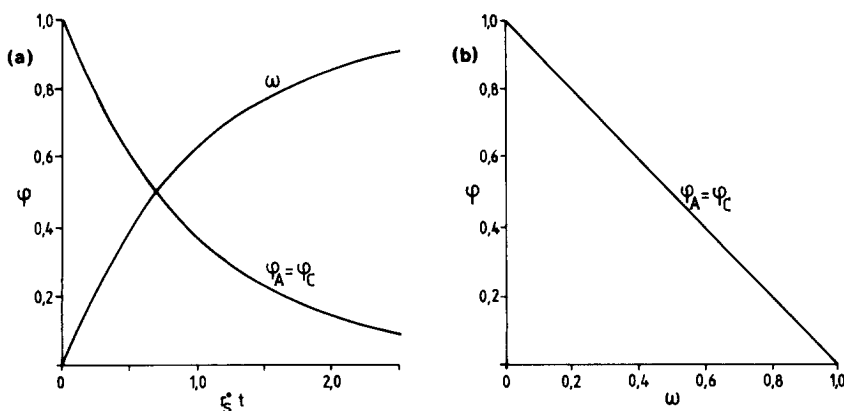
FIG. 1. 1–1 reaction on uniform clusters. (a) Plot of ϕ vs $r_s^0 t$; (b) plot of ϕ vs ω.

pair. Consequently, the deactivation function for a dual site reaction is defined by

$$\varphi_A = \frac{\text{Total number of dual sites still active at coverage } \omega}{\text{Total number of dual sites at zero coverage}} \quad (10)$$

The degree of coverage is still defined as in Eq. (6).

Assuming the coverage of sites by coke on the catalyst surface to be a random process, the coverage of $n - i$ sites in a n-cluster leaving i sites free can occur in $\binom{n}{i}$ ways. The probability of the event of coverage of $n - i$ sites is $S^i(1 - S)^{n-i}$. Therefore, P_{ni}, the probability of occurrence of a n-cluster containing i free sites at time t or coverage $\omega = 1 - i/n$, is the product of the number of ways the event can occur and of the probability of its occurrence:

$$P_{ni} = \binom{n}{i} S^i(1 - S)^{n-i}$$

$$\text{with } i = 0, 1, 2, \ldots n. \quad (11)$$

S still represents the probability that a site is not covered with coke, as in Eq. (3).

The number of n-clusters containing i free sites at time t is

$$N_c(n, i) = \frac{\sigma' A_S}{n} P_{ni}. \quad (12)$$

The total number of sites still free on a catalyst surface at time t, when the coverage is ω, can be written

$$N_s(t) = \frac{\sigma' A_S}{n} \sum_{i=1}^{n} i P_{ni}. \quad (13)$$

The total number of possible dual sites on a catalyst surface at time zero, when the coverage is zero, follows from

$$N_d(t = 0) = \binom{n}{2} \frac{\sigma' A_S}{n}$$

$$= \frac{n - 1}{2} \sigma' A_S \quad (14)$$

and the total number of possible dual sites

left at time t and coverage ω follows from

$$N_d(t) = \sum_{i=2}^{n} \binom{i}{2} N_c(n, i)$$

$$= \frac{\sigma' A_S}{n} \sum_{i=2}^{n} \binom{i}{2} P_{ni}. \quad (15)$$

From Eqs. (10), (14), and (15), the deactivation function for the main reaction becomes

$$\varphi_A = N_d(t)/N_d(t = 0) = S^2. \quad (16)$$

The deactivation function for the coking reaction, as defined by Eq. (5) and accounting for Eq. (13) becomes

$$\varphi_C = \frac{N_s(t)}{\sigma' A_S} = S, \quad (17)$$

and the degree of coverage becomes

$$\omega = \frac{1}{\sigma' A_S} [\sigma' A_S - N_s(t)] = 1 - S. \quad (18)$$

S in Eqs. (16), (17), and (18) is given by Eqs. (3) or (4), since the coking reaction occurs on a single site.

After substitution of Eq. (18) into Eqs. (16) and (17), the deactivation functions can be written in terms of the coverage:

$$\varphi_A = (1 - \omega)^2 \quad (19)$$

$$\varphi_C = 1 - \omega. \quad (20)$$

φ_A now differs from φ_C and is no longer linearly related to ω, whereas φ_C still is. Figure 2a shows the variation of the deactivation functions and the degree of coverage with the reduced time for a given gas phase composition. Figure 2b shows the dependence of the deactivation functions on the degree of coverage. The relations for φ_A and φ_C with respect to ω are unique, i.e., independent of cluster sizes.

A deactivation function that varies nonlinearly with the surface coverage was obtained by Herington and Rideal (3) in their study of the effect of poisoning on a multisite reaction. They dealt with evenly spaced sites and randomly generated ad-
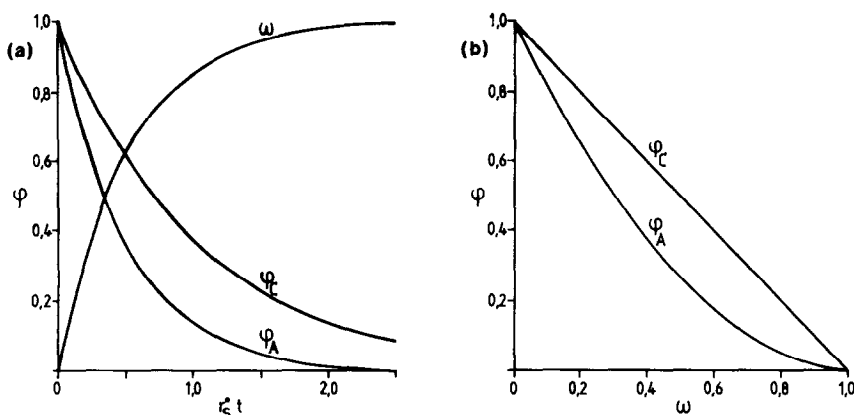
FIG. 2. 2–1 reaction on uniform clusters. (a) Plot of ϕ vs $r_s^\circ t$; (b) plot of ϕ vs ω.

sorption on them of the poison and reacting molecules.

Case III. Main Reaction on a Single Site and Coking Reaction on Dual Sites (1–2 Reaction)

The probability that a site is still active—in the sense defined for a dual-site reaction mechanism—at time $t + dt$ is the product of two probabilities. The first is the probability that a site is active, i.e., still free of coke at time t; the second is the probability that the site is not covered in the time interval dt. The latter is derived from the probability that a site is covered during the time interval dt, namely $r_s^\circ dt$, provided that the site has a neighbor which is not covered and with which it can form a dual site at time t. This can be represented by $D(t)r_s^\circ dt$ in which $D(t)$ is the probability that at least two free sites exist in the cluster. In mathematical terms,

$$S(t + dt) = S(t) + (dS/dt)dt$$
$$= S(t)(1 - D(t)r_s^\circ dt)$$

so that

$$S(t) = \exp\left(- \int_0^t D(t)r_s^\circ dt\right) \quad (21)$$

Two types of mechanisms for the dual-site coking reaction are considered, as shown in Table 1.

Type 1 coking. In this case, only the

coking reaction, not the main reaction, can be completely deactivated, since at least one site in the cluster can never be covered with coke. To account for this behavior, one of the sites in the cluster is excluded from the calculation of the probability representing the distribution of free sites in a cluster. P_{ni} is thus reduced to $P_{n-1,i-1}$. The excluded site is accounted for in the number of free sites.

The probability of the occurrence of a n-cluster containing i free sites is

$$P_{ni} = P_{n-1,i-1} = \binom{n-1}{i-1}S^{i-1}(1 - S)^{n-i}. \quad (22)$$

The probability of there being only one site left free in the cluster at time t is $(1 - S)^{n-1}$, so that

$$D(t) = 1 - (1 - S)^{n-1}. \quad (23)$$

Combining Eqs. (21) and (23) allows the calculation of $S(t)$.

Following the developments for the 2–1 case and using Eqs. (5), (6), (10), and (22), the deactivation function for the main reaction now becomes

$$\varphi_A = \frac{1}{\sigma' A_S}\left(\frac{\sigma' A_S}{n}\sum_{i=1}^{n} iP_{ni}\right)$$
$$= \frac{1}{n} + \frac{n-1}{n}S, \quad (24)$$

and the deactivation function for the dual-site coking reaction becomes

$$\varphi_C = \frac{1}{N_d(t=0)} \left[\frac{\sigma' A_S}{n} \sum_{i=2}^{n} \binom{i}{2} P_{ni} \right]$$

$$= \frac{2}{n} S + \frac{n-2}{n} S^2. \tag{25}$$

The degree of coverage is obtained from

$$\omega = \frac{1}{\sigma' A_S} \left[\frac{\sigma' A_S}{n} \sum_{i=1}^{n} (n-i) P_{ni} \right]$$

$$= \frac{n-1}{n} (1 - S). \tag{26}$$

S in Eqs. (24), (25), and (26) is given by Eq. (21), since the coking reaction involves dual sites.

Combining Eqs. (24) and (25) with Eq. (26) leads to

$$\varphi_A = 1 - \omega \tag{27}$$

$$\varphi_C = 1 - 2\omega + \frac{n(n-2)}{(n-1)^2} \omega^2. \tag{28}$$

Eq. (28) indicates that the rate of the coking reaction approaches zero, although a fraction $1/n$ of the total number of sites is not covered with coke.

Figure 3a shows φ_A and φ_C vs the reduced time for a given gas phase composition. The deactivation now depends on the number of sites in the cluster. φ_A tends to a value of $1/n$ and φ_C tends to zero. The plot of ω vs $r_S^0 t$ is a mirror image of φ_A vs $r_S^0 t$ with respect to the abcissa. As shown in Fig. 3b,

when plotted vs ω, φ_C depends on the number of sites in the cluster but not on φ_A. The variation of φ_C with ω is linear for $n = 2$ but nonlinear for $n > 2$. The larger the number of sites in a cluster, the more pronounced the nonlinearity. The value of φ_C tends asymptotically to $(1 - \omega)^2$, as in the phenomenological approach. On the other hand, φ_A varies linearly with ω, as in the single-site coking mechanism.

Type 2 coking. Separate deviations of the deactivation functions for even and odd numbers of sites in the cluster are required with this type of coking.

(1) Even number of sites in the cluster. In this case, all the sites in the cluster can be covered with coke, so that the probability that a site is not covered with coke at time t equals the probability that two sites are not covered with coke at time t. Therefore, the probability of the occurrence of a cluster of size n containing i free sites can be reduced to that of the occurrence of a cluster of size $n/2$ containing $i/2$ free sites:

$$P_{ni} = P_{n/2,i/2} = \binom{n/2}{i/2} S^{i/2}(1 - S)^{(n-i)/2}, \tag{29}$$

where n is an even integer equal to or exceeding 2.

Following the developments of the previous section with Eqs. (5), (6), (10), and (29), the deactivation function for the main reaction becomes
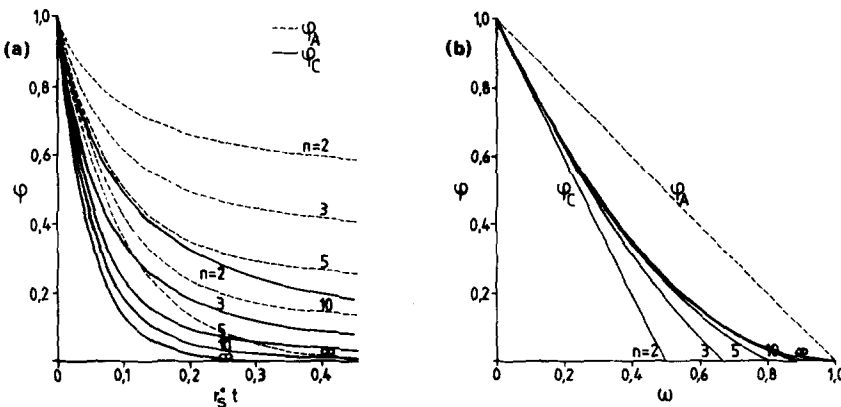

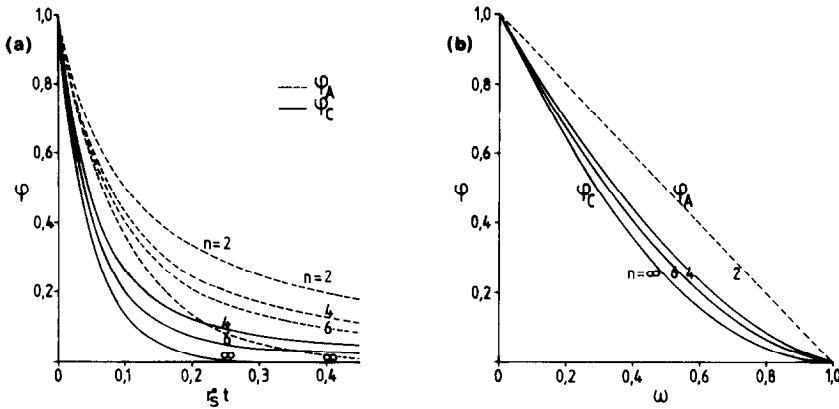FIG. 3. 1–2 reaction on uniform clusters: Type 1 coking mechanism. (a) Plot of ϕ vs $r_S^0 t$; (b) plot of ϕ vs ω.

FIG. 4. 1–2 reaction on uniform clusters containing an even number of sites: Type 2 coking mechanism. (a) Plot of ϕ vs $r_s^o t$; (b) plot of ϕ vs ω.

$$\varphi_A = \frac{1}{\sigma' A_S} \left[\frac{\sigma' A_S}{n} \sum_{i=2}^{n} i P_{ni} \right] = S \quad (30)$$

and that for the coking reaction

$$\varphi_C = \frac{2}{(n-1)\sigma' A_S} \left[\frac{\sigma' A_S}{n} \sum_{i=2}^{n} \binom{i}{2} P_{ni} \right]$$

$$= \frac{S}{n-1} + \frac{n-2}{n-1} S^2, \quad (31)$$

while the degree of coverage is written

$$\omega = \frac{1}{\sigma' A_S} \left[\frac{\sigma' A_S}{n} \sum_{i=2}^{n} (n-1) P_{ni} \right] = 1 - S, \quad (32)$$

where S in Eqs. (30), (31), and (32) is given by Eq. (21). The probability that all sites in the cluster are covered with coke at time t is $(1 - S)^{n/2}$, so that

$$D(t) = 1 - (1 - S)^{n/2}. \quad (33)$$

The variables φ_A, φ_C, and ω can then be expressed in terms of a reduced time $r_s^o t$. Substituting Eq.(32) into Eqs. (30) and (31) leads to

$$\varphi_A = 1 - \omega \quad (34)$$

$$\varphi_C = 1 - \frac{2n-3}{n-1} \omega + \frac{n-2}{n-1} \omega^2. \quad (35)$$

Figure 4 shows the relations of φ_A and φ_C with $r_s^o t$ and ω, respectively. With $n = 2$, $\varphi_C = 1 - \omega = \varphi_A$. When n tends to infinity, $\varphi_C = (1 - \omega)^2$, as shown in Fig. 4b. Again

the rate of deactivation depends on the cluster size. In the plot of φ_C vs ω, however, the dependence with respect to n is reversed.

(2) Odd number of sites in the cluster. In this case, one of the sites in the cluster cannot be covered with coke. Then, the probability of the occurrence of a cluster containing i free sites in a group of n sites becomes

$$P_{ni} = P_{(n-1)/2,(i-1)/2}$$

$$= \binom{\frac{n-1}{2}}{\frac{i-1}{2}} S^{(i-1)/2} (1 - S)^{(n-i)/2}, \quad (36)$$

where n and i are odd integers equal to or exceeding 3. Equation (36) indicates that the probability that a site which can be covered with coke is not covered at time t is equal to the probability that two free sites are not covered at time t.

Combining Eqs. (5), (6), (10), and (36), the deactivation functions and the degree of coverage become

$$\varphi_A = \frac{1}{\sigma' A_S} \left[\frac{\sigma' A_S}{n} \sum_{i=1}^{n} i P_{ni} \right]$$

$$= 1/n + (1 - 1/n)S \quad (37)$$

$$\varphi_C = \frac{2}{(n-1)\sigma' A_S} \left[\frac{\sigma' A_S}{n} \sum_{i=3}^{n} \binom{i}{2} P_{ni} \right]$$

$$= \frac{3}{n} S + \frac{n-3}{n} S^2 \quad (38)$$

$$= \frac{1}{\sigma' A_S} \left[\frac{\sigma' A_S}{n} \sum_{i=3}^{n} (n - i) P_{ni} \right]$$

$$= (1 - 1/n)(1 - S). \qquad (39)$$

S in Eqs. (37), (38), and (39) is given by Eq. (21). $D(t)$ is the probability that only one site is left free in the cluster:

$$D(t) = 1 - (1 - S)^{(n-1)/2} \qquad (40)$$

Substituting Eq. (39) into Eqs. (37) and (38) leads to

$$\varphi_A = 1 - \omega \qquad (41)$$

$$\varphi_C = 1 - \frac{2n - 3}{n - 1} \omega + \frac{n(n - 3)}{(n - 1)^2} \omega^2. \qquad (42)$$

Figures 5a and 5b represent the dependence of the deactivation functions on time and the degree of coverage, respectively. The main reaction maintains a significant level of activity, while the activity for coking approaches zero, even though quite a few sites are not covered yet. For clusters containing an infinite number of sites, φ_C becomes $(1 - \omega)^2$, as expected.

Curves for odd or even numbers of sites nearly coincide at low ω, which is logical, but at high coverages the behavior is opposite.

Case IV: Both Reactions on a Dual Site (2-2 Reaction)

Since both reactions occur on dual sites, both deactivation functions for this case are

identical to φ_C for the 1-2 reaction with the corresponding types of coking. Therefore, the dependence of the deactivation functions on reduced time and on the degree of coverage are identical to those of φ_C for 1-2 reactions, as shown in Figs. 3a, 3b, 4a, 4b, 5a and 5b.

DISTRIBUTION OF CLUSTER SIZES

Since the total number of sites on a catalyst surface is large, whereas a cluster consists of a relatively small number of sites, the Poisson probability distribution seems appropriate to describe the initial distribution of clusters on a catalyst surface. The development of the relations is illustrated here only for Case III, 1-2 reactions with Type 1 coking. Equation (22) now becomes

$$P_{ni} = P_{n-1,i-1}$$
$$= W_n \binom{n-1}{i-1} S^{i-1} (1 - S)^{n-i}, \qquad (43)$$

where W_n is the probability of occurrence of a cluster containing n sites,

$$W_n = \frac{(\sigma' A_k)^n}{n!} \exp(-\sigma' A_k), \qquad (44)$$

and $\sigma' A_k$ is the mean number of sites in a cluster. Following the developments given above and referring to Eqs. (5), (10), and (43), the deactivation functions now become
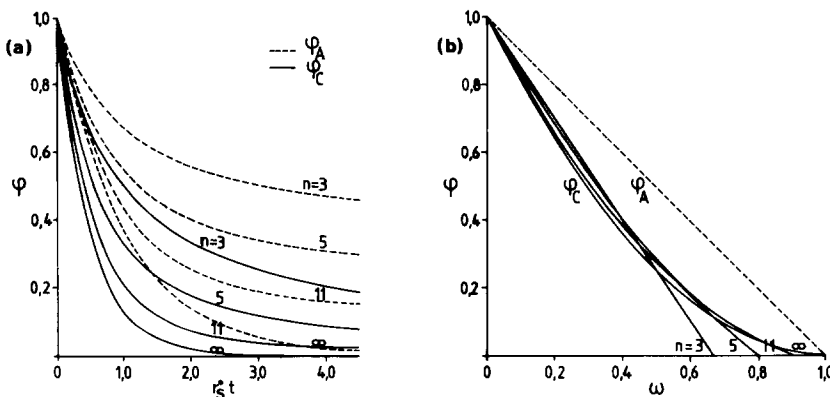

FIG. 5. 1-2 reaction on uniform clusters containing an odd number of sites: Type 2 coking mechanism. (a) Plot of ϕ vs $r_s^o t$; (b) plot of ϕ vs ω.

$$\varphi_A = \frac{1}{\sigma' A_S} \left(\frac{A_S}{A_k} \sum_{n=1}^{\infty} \sum_{i=1}^{n} i P_{ni} \right)$$

$$= \frac{\exp(-\sigma' A_k)}{\sigma' A_k} \{ \exp(\sigma' A_k) - 1$$

$$+ S[(\sigma' A_k - 1) \exp(\sigma' A_k) + 1] \} \quad (45)$$

$$\varphi_C = \frac{1}{N_d(t=0)} \left(\frac{A_S}{A_k} \sum_{n=2}^{\infty} \sum_{i=2}^{n} \binom{i}{2} P_{ni} \right)$$

$$= \frac{2 \exp(-\sigma' A_k)}{(\sigma' A_k)^2} \left\{ (\sigma' A_k - 1) S \right.$$

$$\left. \exp(\sigma' A_k) + S + \frac{S^2}{2} X \right\}, \quad (46)$$

where $X = \exp(\sigma' A_k)[(\sigma' A_k)^2 - 2\sigma' A_k + 2] - 2$. The degree of coverage is given by

$$\omega = \frac{1}{\sigma' A_S} \left[\frac{A_S}{A_k} \sum_{n=1}^{\infty} \sum_{i=1}^{n} (n - i) P_{ni} \right]$$

$$= \frac{\exp(-\sigma' A_k)}{\sigma' A_k} (1 - S)$$

$$[(\sigma' A_k - 1) \exp(\sigma' A_k) + 1]. \quad (47)$$

S in Eqs. (45), (46), and (47) is given by Eq. (21) for dual-site coking.

The probability of having a neighboring site with which to form a pair, $D(t)$, is obtained from two probabilities: the first is the probability that there is a cluster, $1 - P_0$, the second is the probability that only one site is left uncovered:

$$D(t) = 1 - P_0 - \sum_{n=1}^{\infty} P_{n1}$$

$$= 1 - \frac{1}{1 - S} [\exp(-\sigma' A_k S)$$

$$- S \exp(-\sigma' A_k)]. \quad (48)$$

Substitution of Eq. (47) into Eqs. (45) and (46) leads to

$$\varphi_A = 1 - \omega$$

$$\varphi_C = \frac{2 \exp(-\sigma' A_k)}{(\sigma' A_k)^2}$$

$$\left[YZ \exp(\sigma' A_k) + \frac{X}{2} Z^2 \right], \quad (49)$$

where $Y = \exp(-\sigma' A_k)[(\sigma' A_k - 1)\exp(\sigma' A_k) + 1]$ and $Z = 1 - (\sigma' A_k \omega / Y)$.

The behavior of these is entirely analo-
gous to that shown in Figs. 3a and 3b except that for $\sigma' A_k = 2$ a weak curvature develops in the φ_C vs ω relation, whereas for $n = 2$ in Fig. 3b a straight line is obtained.

DISCUSSION

Table 2 contains all the stochastically derived φ vs ω relations and compares them with the corresponding phenomenological ones, which are based on the assumption that there is no restriction on the availability of dual sites. Both approaches evidently lead to identical expressions when the coking occurs on single sites, but not when dual (or multiple) sites are required for the coking. As the number of sites in a cluster increases, the stochastically derived deactivation functions must approach the phenomenological results. The number of sites required to achieve this is not small, however, as is illustrated in Fig. 6.

Figs. 1a and 2a illustrate that when the coking requires single sites only, the deactivation rates are independent of the cluster size, even when the main reaction occurs on dual sites.

When the coking reaction requires dual sites the deactivation rates of both the main and the coking reaction and also the rate of site coverage increase with the cluster size, as shown in Figs. 3a, 4a, and 5a. These results may be linked to observations made on the deactivation of metal-loaded catalysts. Clusters containing a large number of sites are more likely in large metal crystallites, corresponding to a poor dispersion of the metal. The above results may then be interpreted as "the lower the metal dispersion the higher the deactivation rate." Barbier et al. (4), Fuentes et al. (5) and Lankhorst et al. (6) experimentally observed such a trend for the coking reaction on Pt/Al$_2$O$_3$, the cyclopentane conversion over Rh/Al$_2$O$_3$, and the reforming of hexane over Pt/Al$_2$O$_3$ and therefore labeled them as structure sensitive. Whether the rates of deactivation of the main and the coking reaction are structure sensitive or not depends entirely, according to the the-

TABLE 2

A Comparison of the Results of the Stochastic and Phenomenological Models

Reactions	Deactivation functions	Stochastic Model			Phenomenological model
		Uniform clusters		Distribution of clusters	
$1-1^a$	φ_A φ_C	$1 - \omega$		$1 - \omega$	$1 - \omega$
$2-1$	φ_A	$(1 - \omega)^2$		$(1 - \omega)^2$	$(1 - \omega)^2$
	φ_C	$1 - \omega$		$1 - \omega$	$1 - \omega$
$1-2$		Type 1 coking	Type 2 coking	Type 1 coking	
	φ_A	$1 - \omega$	$1 - \omega$	$1 - \omega$	$1 - \omega$
	φ_C	$1 - 2\omega + \dfrac{n(n-2)}{(n-1)^2}\omega^2$	Even number: $1 - \dfrac{2n-3}{n-1}\omega + \dfrac{n-2}{n-1}\omega^2$ Odd number: $1 - \dfrac{2n-3}{n-1}\omega + \dfrac{n(n-3)}{(n-1)^2}\omega^2$	$\dfrac{2\exp(-\sigma'A_k)}{(\sigma'A_k)^2}\left\{YZ\exp(\sigma'A_k) + \dfrac{X}{2}Z^2\right\}^b$	$(1 - \omega)^2$
$2-2^a$	φ_A φ_C	Same as φ_C of 1–2	Same as φ_C of 1–2	Same as φ_C of 1–2	Same as φ_C of 1–2

^{a} Both deactivation functions, φ_A and φ_C, are identical.

^{b} $X = \exp(\sigma'A_k)\{(\sigma'A_k)^2 - 2\sigma'A_k + 2\} - 2$, $Y = \exp(-\sigma'A_k)\{(\sigma'A_k - 1)\exp(\sigma'A_k) + 1\}$, $Z = 1 - (\sigma'A_k\omega/Y)$.

ory developed here, on the coking mechanism: structure sensitivity would develop when the coking reaction requires more than one site. It may be recalled that Boudart (7) conjectured that structure-sensitive reactions require multiple atoms.

It is of importance also to follow the predicted evolution of φ_A and φ_C with the degree of coverage, ω. Indeed, deactivation studies carried out in an electrobalance

enable φ_C to be related to the coke content (1). The coke content is a measure of the degree of site coverage, provided that coke does not grow on already deposited coke, or, if it does, provided that all the coke particles have the same size (2, 8–10). When both the main and the coking reaction occur on single sites, φ_A and φ_C coincide and vary linearly with ω. For 2–1 reactions φ_C and φ_A vary in a different way
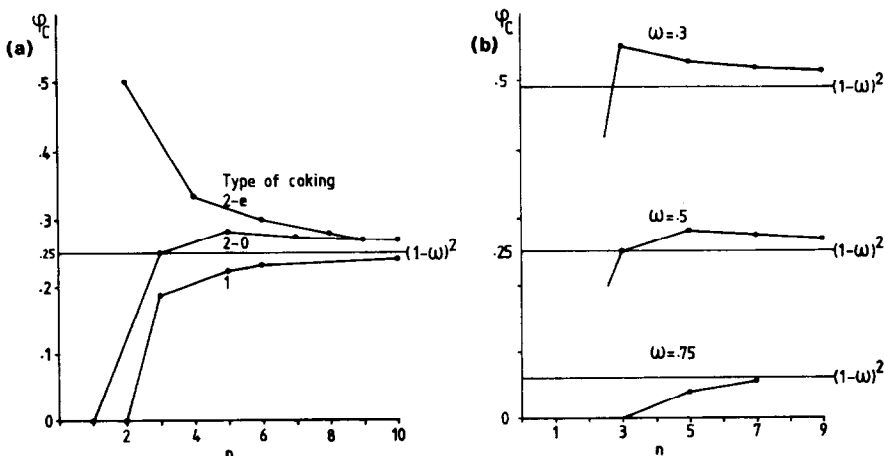

FIG. 6. Dependence of ϕ_c on the number of sites in uniform clusters for 1–2 reactions. (a) Type 1 and Type 2 coking at $\omega = 0.5$; (b) Type 2 coking with an odd number of sites at various values of ω.

with respect to ω. For 1–2 reactions φ_C differs from φ_A and develops a dependence on the cluster size; φ_A, however, is unique and varies linearly with ω. For 2–2 reactions φ_A becomes identical with φ_C.

For dual- (or multi-) site coking, the behavior of φ_C with respect to ω—or the coke content, with the restrictions mentioned above—depend on the type of coking. For Type 1 dual-site coking, in which the sites are permanently covered one by one but counted per pair for calculation of φ_C, not all the sites in the cluster can be covered. The φ_C curves in Fig. 3b intersect the abcissa at ω values of $1 - 1/n$. A value of $\omega = 1$ can be reached only for n tending toward infinity. This means that for $n = \infty$ the coke content reaches a limit and that φ_A does not drop below a certain value, e.g., 0.34 for $n = 3$. At $\omega = 0$, or very low coverage, the slopes of the φ_C vs ω curves are independent of n and take a value of -2, as can be seen from Eq. (28). With increasing n all the curves are bounded between the straight line corresponding to $n = 2$ and the curve for $n = \infty$, for which $\varphi_C = (1 - \omega^2)$, which is the phenomenological result. Comparing φ_C for the various n at a fixed value of ω reveals that the deactivation of the coking is more pronounced when n decreases, i.e., when the metal dispersion is high, as is also shown in Fig. 6a.

For Type 2 dual-site coking with even number of sites in the cluster, in which the sites are permanently covered pair by pair and counted in pairs for calculation of φ_C, all the sites can be covered, so that ω becomes one and both φ_A and φ_C tend to zero, whatever the value of n (Fig. 4b).

The initial slopes of the φ_C vs ω curves depend on the cluster size. Their value is $3 - 2n/n - 1$, as can be seen from Eq. (35). For $n = 2$, φ_C is a straight line coinciding with φ_A. The initial slope increases with n.

Figure 4b also shows that, for a given ω, the deactivation of the coking is more pronounced when n is increased, i.e., when the dispersion is lowered. This is also illustrated in Fig. 6a.

For Type 2 coking with an odd number of sites at least one site cannot be coked, as in Type 1 coking, and some features of that case are also encountered here. Except for $n = \infty$, the φ_C curves intersect the abcissa for values different from $\omega = 1$, again at $1 - 1/n$. The initial slopes are given by the same formula as for the case with even number of sites, as can be seen from Eq. (42). A straight line is obtained for $n = 3$, with slope -1.5, which is intuitively clear. The limiting curve for $n = \infty$ has a slope of -2, but since the curve tends to zero when ω becomes one the φ_C vs ω curves for various cluster sizes must intersect. At low values of ω the deactivation of the coking is more pronounced when n is large, as for even numbers (Fig. 6b). At high values of ω, however, because the curves intersect, a feature of Type 1 coking recurs: the deactivation of the coking is more pronounced when n is small (Fig. 6b).

Summarizing, the sensitivity of the deactivation of a dual-site coking reaction with respect to the degree of site coverage depends not only on the type of coking but also on the number of sites in the cluster: with Type 1 coking the sensitivity of φ_C vs ω is increased as n is decreased; with Type 2 coking it increases with n (even or odd), except when n is odd and ω takes on high values. These are effects that cannot be predicted by the phenomenological approach. Notice also that, whatever the coking mechanism, the deactivation function, φ_A, for a single-site main reaction varies linearly with the degree of coverage and is independent of n.

CONCLUSION

The stochastic approach to the formulation of catalyst deactivation by site coverage presented here provides considerably more insight into the phenomenon than the approach used until now. Coking reactions are often multi-site reactions and the phenomenological approach may not be sufficiently accurate for such a situation. The results arrived at by the stochastic approach may provide valuable guidelines in

the design of better catalysts, less subject to deactivation by decreasing the surface density of the sites. The ensemble theory proposed as an explanation for the improvement of monometallic catalysts by the addition of a second metal, as practiced in catalytic reforming, is a qualitative illustration of the results derived here.

Finally, it should be added that the approach developed here is directly applicable to catalyst deactivation by poisons. Combined with the model for the deactivation by pore blockage ($2a$), the present theory opens the way to a more rigorous description of the deactivation encountered in resid hydrotreating, in which both metal components and coke are responsible for the catalyst decay.

APPENDIX: NOMENCLATURE

A, B, C   Reactant, product, and coke, respectively
A_S Total catalyst surface area, m^2
A_k Critical surface area where multisite reaction can occur, m^2
C_t Total concentration of reaction sites, kmol/kg catalyst
C_{Cl} Concentration of sites covered with coke, kmol/kg catalyst
$D(t)$ Probability that at least two sites exist in a cluster at time t
i Number of free sites in a cluster
l Reaction site
n Number of sites in a cluster
n_A Number of sites involved in the main reaction
n_C Number of sites involved in the coking reaction
$N_c(n, i)$ Number of clusters containing i free sites out of n initial sites at time t
N_s Total number of sites on a catalyst surface
N_d Total number of dual sites on catalyst surface
P_n Probability that n reaction sites are existing in a cluster at time zero

P_{ni} Probability of the occurrence of a n-cluster containing i free sites at time t corresponding to coverage ω
P_0 Probability of having an "empty" cluster
r_s° Initial rate of fractional site coverage by coke, 1/hr
S Probability that a site is not covered with coke at time t time, hr
W_n Probability of occurrence of a cluster containing n sites
σ' Site density based on catalyst surface area, m^{-2}
φ_A Deactivation function for the main reaction
φ_C Deactivation function for the coking reaction
ω Degree of site coverage

REFERENCES

1. Froment, G. F., *Proc. Int. Congr. Catal. 6th, London,* 10, 1976.
2a. Beeckman, J. W., and Froment, G. F., *Ind. Eng. Chem. Fundam.* 18, 245 (1979).
2b. Beeckman, J. W., and Froment, G. F., *Chem. Eng. Sci.* 35, 805 (1980).
2c. Beeckman, J. W., and Froment, G. F., *Ind. Eng. Chem. Fundam.* 21, 243 (1982).
3. Herington, E. F. G., and Rideal, E. K., *Trans. Faraday Soc.* 40, 505 (1944).
4. Barbier, J., Corro, G., Zhang, Y., Bournonville, J. P., and Franck, J. P., *Appl. Catal.* 13, 245 (1985).
5. Fuentes, S., Figueras, F., and Gomez, R., *J. Catal.* 68, 419 (1981).
6. Lankhorst, P. P., de Jongste, H. C., and Ponec, V., *in* "Catalyst Deactivation" (B. Delmon and G. F. Froment, Eds.), p. 43. Elsevier Scientific, Amsterdam, 1980.
7. Boudart, M., *Proc. Int. Congr. Catal. 6th, London,* 1, 1976.
8. Froment, G. F., *in* "Catalyst Deactivation" (B. Delmon and G. F. Froment, Eds.), p. 1. Elsevier Scientific, Amsterdam, 1980.
9. Froment, G. F., *in* "Progress in Catalyst Deactivation" (J. Figueiredo, Ed.), p. 103. Nijhoff, Den Haag, 1982.
10. Froment, G. F., Actas do 9° Symposio Iberoamericano de Catalise, Lisboa, July 1984.