MODELING OF HETEROGENEOUS REACTION KINETICS: A STOCHASTIC APPROACH

In-Sik NAM* and Young Gul KIM

Department of Chemical Engineering, Pohang Institute of Science & Technology (POSTECH),
P.O. Box 125, Pohang 790-330, Korea
(Received 10 October 1988 • accepted 18 January 1989)

Abstract—A stochastic model representing the state of the catalyst surface is developed for several possible reaction mechanisms. With the pseudo-steady state assumption, the fresh catalyst solution was used for the initial value of deactivating system. The deactivation functions obtained from the present study shows a good agreement with the model proposed by Nam and Froment[1].When the reaction requires more than one site, the reaction becomes structure sensitive. However, for a single site reaction requiring one site only, the reaction belongs to the class of structure-insensitive reaction. Deactivation reactions can also be classified by this manner.

INTRODUCTION

Since Hougen and Watson [2] developed a phenomenological kinetic model based upon the site balance suggested by the reaction mechanism, modeling of chemical reaction on heterogeneous catalysis has been usefully employed as a tool in the chemical reactor design. For the final rate model, the number of reaction sites involved are deterministically counted which randomly adsorb the reaction molecules during the course of the reaction at equilibrium. However, the number of participating reaction sites on the catalyst surface can be altered by the reaction mechanisms and by the catalyst deactivation which are quite common processes in heterogeneous catalysis. Indeed, the reaction kinetics by multi site mechanism is further complicated by deactivation.

Froment [3] introduced the probability of nearest neighboring site to describe the deactivating reaction kinetics by dual site mechanism using Hougen-Watson formalism. However, a single term for the probabilities of the dual site formation and of the deactivation cannot be estimated by the formalism due to their unmeasurable characteristics.

The most appealing approach to incorporate these probabilities into reaction kinetics may be the statistic analysis of the state of the reaction sites on the catalyst surface. Although these probabilities can be calculated by the method of random number generation through the determination of individual steps of adsorption or reaction not specified by the given reaction mechanism [4,5], the exclusive form of kinetic expression cannot be derived which is the ultimate goal of kinetic modeling. On the other hand, Fredrickson [6] stochastically described the system of triangular reaction by a closed collection of N objects, with each object having three possible states. The transition of an object from one state to another occurs in x stochastic ways and is independent of the state of the other objects.

In the present study, a stochastic approach is developed which can predict the reaction rates depending upon the state of sites on the catalyst surface by the application of Fredrickson's transition theory. The developed stochastic model specified by the given reaction mechanisms provides not only a mechanistic insight into the single or dual site reactions but also a better understanding of primary and deactivation kinetics. For instance, the phenomenological kinetic model describes the course of the reaction, but the stochastic model can describe the transition state of reaction permiting the inclusion of the probabilities of multi site formation and of catalyst deactivation into the kinetic modeling for fresh and deactivating catalytic system.

The model developed in this study is based on a cluster of reaction sites on catalyst surface. The cluster of reaction sites which is extensively described by Nam and Froment [1] is defined as a set of sites on the catalyst surface which are sufficiently close to each other to form the multi site required for the given reaction.

---

* Author to whom correspondences should be addressed.

THEORETICAL DEVELOPMENT

Uniform cluster size over the catalyst surface indicating that the reaction rates of each cluster are identical is assumed. Possible reaction mechanisms for the simple reversible reaction, $A \rightleftharpoons B$ are presented in Table 1. Two types of dual site reaction mechanism and coking as a deactivation reaction are considered in the present study.

The state of cluster containing n number of sites is characterized by the probability $P(l_i, Al_j, Bl_k, Cl_m)$ that in the cluster at time t: there exist i free reaction sites, j reaction sites reversibly adsorbed by A, k reaction sites reversibly adsorbed by B and m sites irreversibly covered with coke (i, j, k, and m are integers including zero and the summation of these integers has to be n).
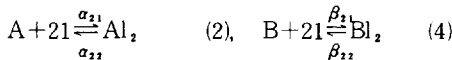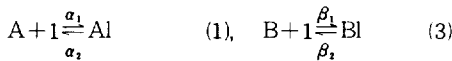
Based upon the multiplication law of probabilities: $P(l_i, Al_j, Bl_k, Cl_m)_{t+dt} = P(l_i, Al_j, Bl_k, Cl_m)_t \cdot P$[probability that no reactions occur during the time interval dt] + P[probability that the combination of (l_i, Al_j, Bl_k, Cl_m) is being formed from other combination in the time interval dt]
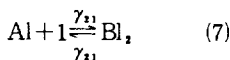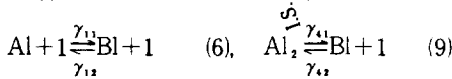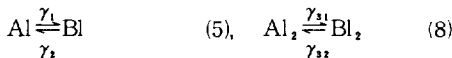
$$P(l_i, Al_j, Bl_k, Cl_m)_{t+dt} = P(l_i, Al_j, Bl_k, Cl_m)_t$$
$$[1 - i(\alpha_1 + \beta_1)dt$$
$$-j(\alpha_2 + \gamma_1 + \eta_1)dt - k(\beta_2 + \gamma_2 + \eta_2)dt$$
$$-\binom{i}{2}(\alpha_{21} + \beta_{21})dt - \binom{j}{2}(\alpha_{22} + \gamma_{31} + \gamma_{41} + \eta_{13}$$
$$+\eta_{14})dt - \binom{k}{2}(\beta_{22} + \gamma_{22} + \gamma_{32} + \eta_{23} + \eta_{24})dt$$
$$-ij(\gamma_{11} + \gamma_{21} + \eta_{11} + \eta_{12})dt$$
$$-ik(\gamma_{12} + \gamma_{42} + \eta_{21} + \eta_{22})dt]$$
$$+P(l_{i+1}, Al_{j-1}, Bl_k, Cl_m)_t (i+1)\alpha_1 dt$$
$$+P(l_{i-1}, Al_{j+1}, Bl_k, Cl_m)_t (j+1)\alpha_2 dt$$
$$+P(l_{i+2}, Al_{j-2}, Bl_k, Cl_m)_t \left[\frac{i+2}{2}\right]\alpha_{21} dt$$
$$+P(l_{i-2}, Al_{j+2}, Bl_k, Cl_m)_t \left(\frac{j+2}{2}\right)\alpha_{22} dt$$
$$+P(l_{i+1}, Al_j, Bl_{k-1}, Cl_m)_t (i+1)\beta_1 dt$$
$$+P(l_{i-1}, Al_j, Bl_{k+1}, Cl_m)_t (k+1)\beta_2 dt$$
$$+P(l_{i+2}, Al_j, Bl_{k-2}, Cl_m)_t \left[\frac{i+2}{2}\right]\beta_{21} dt$$
$$+P(l_{i-2}, Al_j, Bl_{k+2}, Cl_m)_t \left(\frac{k+2}{2}\right)\beta_{22} dt$$
$$+P(l_i, Al_{j+1}, Bl_{k-1}, Cl_m)_t (j+1)\gamma_1 dt$$
$$+P(l_i, Al_{j-1}, Bl_{k+1}, Cl_m)_t (k+1)\gamma_2 dt$$
$$+P(l_i, Al_{j+1}, Bl_{k-1}, Cl_m)_t i(j+1)\gamma_{11} dt$$
$$+P(l_i, Al_{j-1}, Bl_{k+1}, Cl_m)_t i(k+1)\gamma_{12} dt$$
$$+P(l_{i+1}, Al_{j+1}, Bl_{k-2}, Cl_m)_t (i+1)(j+1)\gamma_{21} dt$$
$$+P(l_{i-1}, Al_{j-1}, Bl_{k+2}, Cl_m)_t \left(\frac{k+2}{2}\right)\gamma_{22} dt$$
$$+P(l_i, Al_{j+2}, Bl_{k-2}, Cl_m)_t \left(\frac{j+2}{2}\right)\gamma_{31} dt$$
$$+P(l_i, Al_{j-2}, Bl_{k+2}, Cl_m)_t \left(\frac{k+2}{2}\right)\gamma_{32} dt$$
$$+P(l_{i-1}, Al_{j+2}, Bl_{k-1}, Cl_m)_t \left(\frac{j+2}{2}\right)\gamma_{41} dt$$
$$+P(l_{i+1}, Al_{j-2}, Bl_{k+1}, Cl_m)_t (i+1)(k+1)\gamma_{42} dt$$
$$+P(l_i, Al_{j+1}, Bl_k, Cl_{m-1})_t (j+1)\eta_1 dt$$
$$+P(l_i, Al_{j+1}, Bl_k, Cl_{m-1})_t i(j+1)\eta_{11} dt$$
$$+P(l_{i+1}, Al_{j+1}, Bl_k, Cl_{m-2})_t (i+1)(j+1)\eta_{12} dt$$
$$+P(l_i, Al_{j+2}, Bl_k, Cl_{m-2})_t \left(\frac{j+2}{2}\right)\eta_{13} dt$$
$$+P(l_{i-1}, Al_{j+2}, Bl_k, Cl_{m-1})_t \left(\frac{j+2}{2}\right)\eta_{14} dt$$
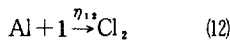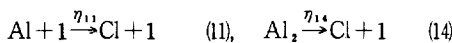
Table 1. Reaction mechanisms for $A \rightleftharpoons B$

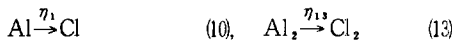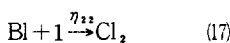○ Adsorption – Desorption of A & B

$$A + 1 \underset{\alpha_2}{\overset{\alpha_1}{\rightleftharpoons}} Al \quad (1), \qquad B + 1 \underset{\beta_2}{\overset{\beta_1}{\rightleftharpoons}} Bl \quad (3)$$

$$A + 21 \underset{\alpha_{22}}{\overset{\alpha_{21}}{\rightleftharpoons}} Al_2 \quad (2), \qquad B + 21 \underset{\beta_{22}}{\overset{\beta_{21}}{\rightleftharpoons}} Bl_2 \quad (4)$$

○ Surface Reactions

$$Al \underset{\gamma_2}{\overset{\gamma_1}{\rightleftharpoons}} Bl \quad (5), \qquad Al_2 \underset{\gamma_{32}}{\overset{\gamma_{31}}{\rightleftharpoons}} Bl_2 \quad (8)$$

$$Al + 1 \underset{\gamma_{12}}{\overset{\gamma_{11}}{\rightleftharpoons}} Bl + 1 \quad (6), \qquad Al_2 \underset{\gamma_{42}}{\overset{\gamma_{41}}{\rightleftharpoons}} Bl + 1 \quad (9)$$

$$Al + 1 \underset{\gamma_{21}}{\overset{\gamma_{21}}{\rightleftharpoons}} Bl_2 \quad (7)$$

○ Parallel Coke Formation

$$Al \overset{\eta_1}{\rightarrow} Cl \quad (10), \qquad Al_2 \overset{\eta_{13}}{\rightarrow} Cl_2 \quad (13)$$

$$Al + 1 \overset{\eta_{11}}{\rightarrow} Cl + 1 \quad (11), \qquad Al_2 \overset{\eta_{14}}{\rightarrow} Cl + 1 \quad (14)$$

$$Al + 1 \overset{\eta_{12}}{\rightarrow} Cl_2 \quad (12)$$

○ Consecutive Coke Formation
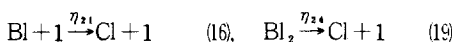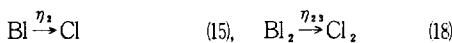
$$Bl \overset{\eta_2}{\rightarrow} Cl \quad (15), \qquad Bl_2 \overset{\eta_{23}}{\rightarrow} Cl_2 \quad (18)$$

$$Bl + 1 \overset{\eta_{21}}{\rightarrow} Cl + 1 \quad (16), \qquad Bl_2 \overset{\eta_{24}}{\rightarrow} Cl + 1 \quad (19)$$

$$Bl + 1 \overset{\eta_{22}}{\rightarrow} Cl_2 \quad (17)$$

$$+P\ (l_{\iota}, Al_{j}, Bl_{k+1}, Cl_{m-1})_{\iota}\ (k+1)\ \eta_{2}dt$$

$$+P\ (l_{\iota}, Al_{j}, Bl_{k+1}, Cl_{m-1})_{\iota}i\ (k+1)\ \eta_{21}dt$$

$$+P\ (l_{\iota+1}, Al_{j}, Bl_{k+1}, Cl_{m-2})_{\iota}\ (i+1)\ (k+1)\ \eta_{22}dt$$

$$+P\ (l_{\iota}, Al_{j}, Bl_{k+2}, Cl_{m-2})_{\iota}\ (\frac{k+2}{2})\ \eta_{23}dt$$

$$+P\ (l_{\iota-1}, Al_{j}, Bl_{k+2}, Cl_{m-1})_{\iota}\ (\frac{k+2}{2})\ \eta_{24}dt \qquad (2)$$

where, i, j. k, m= integers including zero, $i+j+k+m= n$, $\begin{bmatrix} i \\ 2 \end{bmatrix}$ represents number of possible dual sites among vacant sites, i resulting $\frac{i!}{2!\ (i-2)!}$ and $(\frac{i}{2})$, $(\frac{k}{2})$, $(\frac{j+2}{2})$ & $(\frac{k+2}{2})$ represent number of dual sites for A or B occupying two sites such as Al_2 or Bl_2.

As shown in the first term of RHS in eqn (2), the probability that no reaction is taking place in the time in-

terval dt for the site combination of (l_i, Al_j, Bl_k, Cl_m) in the cluster is one minus the probability that reactions listed in Table 1 occur. The multiplication of rate constants by infinitesimal time dt gives the probability that the corresponding reactions occur in the sense of the reaction path. For instance, α_1 dt represents the probability that molecule A adsorbs on free site i in the time interval dt. For the second part of RHS in eqn. (2), only limited numbers of combinations are used because the combinations which require several reactions to attain the combination of (l_i, Al_j, Bl_k, Cl_m) in the time interval dt results in higher power terms of dt. Note that eqn. (2) can be written for any reaction mechanisms assumed.

Rearrangement of eqn.(2) and division by dt finally yields, a differential equation which can describe the probability of the occurrence of the given combination of a cluster.

$$dP\ (l_{\iota}, Al_{j}, Bl_{k}, Cl_{m})/dt = -P\ (l_{\iota}, Al_{j}, Bl_{k}, Cl_{m})\ \{i\ (\alpha_{1}+\beta_{1})+j\ (\alpha_{2}+\gamma_{1}+\eta_{1})$$

$$+k\ (\beta_{2}+\gamma_{2}+\eta_{2})+[\ ^{i}_{2}\ ]\ (\alpha_{21}+\beta_{21})+(^{j}_{2})\ (\alpha_{22}+\gamma_{31}+\gamma_{41}+\eta_{13}+\eta_{14})$$

$$+(\frac{k}{2})\ (\beta_{22}+\gamma_{22}+\gamma_{32}+\eta_{23}+\eta_{24})+ij\ (\gamma_{11}+\gamma_{21}+\eta_{11}+\eta_{12})$$

$$+ik\ (\gamma_{12}+\gamma_{42}+\eta_{21}+\eta_{22})\}$$

$$+(i+1)\alpha_{1}P\ (l_{\iota+1}, Al_{j-1}, Bl_{k}, Cl_{m})+(j+1)\alpha_{2}P\ (l_{\iota-1}, Al_{j+1}, Bl_{k}, Cl_{m})$$

$$+[^{i+2}_{\ \ 2}]\alpha_{21}P\ (l_{\iota+2}, Al_{j-2}, Bl_{k}, Cl_{m})+(\frac{j+2}{2})\alpha_{22}P\ (l_{\iota-2}, Al_{j+2}, Bl_{k}, Cl_{m})$$

$$+(i+1)\beta_{1}P\ (l_{\iota+1}, Al_{j}, Bl_{k-1}, Cl_{m})+(k+1)\beta_{2}P\ (l_{\iota-1}, Al_{j}, Bl_{k+1}, Cl_{m})$$

$$+[^{i+2}_{\ \ 2}]\beta_{21}P\ (l_{\iota+2}, Al_{j}, Bl_{k-2}, Cl_{m})+(\frac{k+2}{2})\beta_{22}P\ (l_{\iota-2}, Al_{j}, Bl_{k+2}, Cl_{m})$$

$$+(j+1)\gamma_{1}P\ (l_{\iota}, Al_{j+1}, Bl_{k-1}, Cl_{m})+(k+1)\gamma_{2}P\ (l_{\iota}, Al_{j-1}, Bl_{k+1}, Cl_{m})$$

$$+i\ (j+1)\gamma_{11}P\ (l_{\iota}, Al_{j+1}, Bl_{k-1}, Cl_{m})+i\ (k+1)\gamma_{12}P\ (l_{\iota}, Al_{j-1}, Bl_{k+1}, Cl_{m})$$

$$+(i+1)\ (j+1)\gamma_{21}P\ (l_{\iota+1}, Al_{j+1}, Bl_{k-2}, Cl_{m})+(\frac{k+2}{2})\gamma_{22}P\ (l_{\iota-1}, Al_{j-1}, Bl_{k+2}, Cl_{m})$$

$$+(\frac{j+2}{2})\gamma_{31}P\ (l_{\iota}, Al_{j+2}, Bl_{k-2}, Cl_{m})+(\frac{k+2}{2})\gamma_{32}P\ (l_{\iota}, Al_{j-2}, Bl_{k+2}, Cl_{m})$$

$$+(\frac{j+2}{2})\gamma_{41}P\ (l_{\iota-1}, Al_{j+2}, Bl_{k-1}, Cl_{m})+(i+1)\ (k+1)\gamma_{42}P\ (l_{\iota+1}, Al_{j-2}, Bl_{k+1}, Cl_{m})$$

$$+(j+1)\eta_{1}P\ (l_{\iota}, Al_{j+1}, Bl_{k}, Cl_{m-1})+i\ (j+1)\eta_{11}P\ (l_{\iota}, Al_{j+1}, Bl_{k}, Cl_{m-1})$$

$$+(i+1)\ (j+1)\eta_{12}P\ (l_{\iota+1}, Al_{j+1}, Bl_{k}, Cl_{m-2})+(\frac{j+2}{2})\eta_{13}P\ (l_{\iota}, Al_{j+2}, Bl_{k}, Cl_{m-2})$$

$$+(\frac{j+2}{2})\eta_{14}P\ (l_{\iota-1}, Al_{j+2}, Bl_{k}, Cl_{m-1})+(k+1)\eta_{2}P\ (l_{\iota}, Al_{j}, Bl_{k+1}, Cl_{m-1})$$

$$+i\ (k+1)\eta_{21}P\ (l_{j}, Al_{j}, Bl_{k+1}, Cl_{m-1})+(i+1)\ (k+1)\eta_{22}P\ (l_{\iota+1}, Al_{j}, Bl_{k+1}, Cl_{m-2})$$

$$+(\frac{k+2}{2})\eta_{23}P\ (l_{\iota}, Al_{j}, Bl_{k+2}, Cl_{m-2})+(\frac{k+2}{2})\eta_{24}P\ (l_{\iota-1}, Al_{j}, Bl_{k+2}, C_{m-1}) \qquad (3)$$

Since the sum of all combinations has to be one at any time, a specific combination can be calculated from the summation of probabilities and one of the number of differential equations may be reduced. The possible combinations of sites in the cluster for $n = 2$ are given by Table 2. Note that the number of combinations is identical to the number of differential equations.

For the overall reaction mechanisms listed in Table 1, the reaction rates of the three main reactions, the rate of deactivation and the degree of coverage by deactivating precursor are given:

Table 2. Combinations of sites for n = 2

Possible Combinations: P1(2,0,0,0), P2(1,1,0,0), P3(0,2,0,0), P4(0,1,1,0), P5(0,0,2,0), P6(0,0,1,1), P7(0,0,0,2), P8(1,0,1,0), P9(1,0,0,1), P10(0,1,0,1)

Reaction Classification	Mechanism Selected from Table 1	Combinations
1-1	1,3,5,10	P1,P2,P3,P4,P5,P6,P7,P8,P9,P10
	or 1,3,5,15	
2-1	a) 1,3,6,10	Same as in 1-1 Reaction
	or 1,3,6,15	
	b) 2,3,9,15	P1,P3,P5,P6,P7,P8,P10
1-2	a) 1,3,5,11	Same as in 1-1 Reaction
	or 1,3,5,16	
	b) 1,3,5,12	P1,P2,P3,P4,P5,P7,P8
	or 1,3,5,17	
2-2	a) 1,3,6,11	Same as in 1-1 Reaction
	or 1,3,6,16	
	b) 1,3,6,17	Same as in b) of 1-2 Reaction
	or 1,3,6,12	
	c) 1,4,7,11	P1,P2,P3,P5,P7,P9,P10
	or 1,4,7,19	
	d) 1,4,7,12	P1,P2,P3,P5,P7
	or 1,4,7,18	
	e) 2,3,9,13	P1,P3,P5,P7,P8
	or 2,3,9,17	
	f) 2,3,9,14	P1,P3,P5,P6,P7,P8,P9
	or 2,3,9,15	
	or 2,3,9,16	
	g) 2,4,8,13	P1,P3,P5,P7
	or 2,4,8,18	
	h) 2,4,8,14	P1,P3,P5,P7,P9
	or 2,4,8,19	

1) Adsorption rate of A

$$r_{A_1} = \frac{1}{N_A} \Sigma \Sigma \Sigma P (I_i, AI_j, BI_k, CI_m)$$

$$\{i\alpha_1 - j\alpha_2 + \binom{i}{2}\alpha_{21} - \binom{j}{2}\alpha_{22}\} \qquad (4)$$

2) Surface reaction rate of A to B

$$r_{A_2} = \frac{1}{N_A} \Sigma \Sigma \Sigma P (I_i, AI_j, BI_k, CI_m)\{j\gamma_1 - k\gamma_2 - ij\gamma_{11}$$

$$- ik\gamma_{22} + ij\gamma_{21} - \frac{k}{2}\gamma_{22} + \frac{j}{2}\gamma_{31} - \frac{k}{2}\gamma_{32} - \frac{j}{2}$$

$$\gamma_{41} - ik\gamma_{42}\} \qquad (5)$$

3) Desorption rate of B

$$r_{A_3} = \frac{1}{N_A} \Sigma \Sigma \Sigma P (I_i, AI_j, BI_k, CI_m) \{i\beta_1 - k\beta_2$$

$$- \binom{i}{2}\beta_{21} - (\frac{k}{2})\beta_{22}\} \qquad (6)$$

4) Coking rate

$$r_c = \frac{1}{N_A} \Sigma \Sigma \Sigma P (I_i, AI_j, BI_k, CI_m) \{j\eta_1 + ij (\eta_{11} + \eta_{12})$$

$$+ \frac{j}{2} (\eta_{13} + \eta_{14}) + k\eta_2 + ik (\eta_{21} + \eta_{22}) + (\frac{k}{2})$$

$$(\eta_{23} + \eta_{24})\} \qquad (7)$$

5) Degree of coverage

$$\omega = \frac{1}{n} \Sigma \Sigma \Sigma P (I_i, AI_j, BI_k, CI_m) m \qquad (8)$$

where $m = n-i-j-k$ and N_A = Avogadro number.

The set of eqns. (4) to (8) permits the determination of reaction rates and the degree of coverage for the given reaction mechanisms. When the rate of coke formation is very slow with respect to the three main reaction rates, then the rate of adsorption of A, surface reaction A to B and desorption of B become identical to each other.

$$r_A = r_{A_1} = r_{A_2} = r_{A_3} \qquad (9)$$

The pseudo-steady state assumption taken in this study is based on the fact that the time scale of catalyst deactivation is many order of magnitude larger than that of the main reaction. For most processes with deactivation time scales of several weeks or more, it is satisfactory to use the probabilities of fresh catalyst as initial values for the numerical solution of the deactivation system.

The deactivation functions for main reaction and coking reaction are given by

$$\varphi_A = (r_A)_t / (r_A)_{t=0} \qquad (10)$$

$$\varphi_c = (r_c)_t / (r_c)_{t=0} \qquad (11)$$

FRESH CATALYST: NO DEACTIVATION

With the pseudo-steady state assumption, the probabilities of the different combinations for fresh catalyst can be calculated by the set of algebraic equation (3) with $d/dt = 0$, η_1, η_{11}, η_{12}, η_{13}, η_{14}, η_2, η_{21}, η_{22}, η_{23} and $\eta_{24} = 0$ and $m = 0$. Other parameters such as α, β and γ employed in this study are given in Fig. 1. The number of equations which is identical to the number of possible combinations of sites in a cluster depends on the reaction mechanism and the cluster size. In order to examine the influence of the cluster sizes on the main reaction rates, Fig. 1 compares the reaction rates for single and dual site with respect to the number of sites in the clusters varying from 1 to 8.

For the single site mechanism where the main reaction occurs on a single site, the reaction rates are linearly proportional to the number of sites in the cluster. For the dual site mechanism where the main reaction occurs on dual sites, the reaction rate is also proportional to the cluster sizes greater than 5. It suggests that the rate of change of the total sites by the introduction of new site to the cluster is constant. It is quite understandable since the new reaction site can not change the state of the surface for the single site reaction and for the dual site reaction with the large number of sites. Indeed, the probability of dual site forma-

tion in the cluster becomes one as the cluster size increases. However, for the smaller cluster of the dual site reaction, the relationship between the reaction rate and the number of reaction sites is no longer linear and even becomes quadratic as shown in Fig. 1(a) for n between 2 and 4. Furthermore, the dual site reaction rate becomes greater than the single site reaction rate when n exceeds 5, since the significant change of the probability for the dual site formation in the cluster is expected from the cluster size 5. It is also observed for phenomenological model that the dual site reaction rate is proportional to the square of the total concentration of reaction sites for the large cluster size, while the single site reaction is simply proportional to the total number of reaction sites on the catalyst surface.

From the standpoint of structure sensitive and insensitive reactions for metal catalyst, the cluster size may correspond to the degree of metal dispersion. In other words, the higher the metal dispersion, the smaller the cluster size. Fig. 1(b) shows that the single site reaction rate per site is independent of the cluster size, indicating the structure insensitivity of the reaction and that the dual site reaction rate per site depends on the cluster sizes revealing the structure sensitive nature of the reaction. It should be noted that the reaction site employed in this study may be different from the metal atoms of metal catalyst.
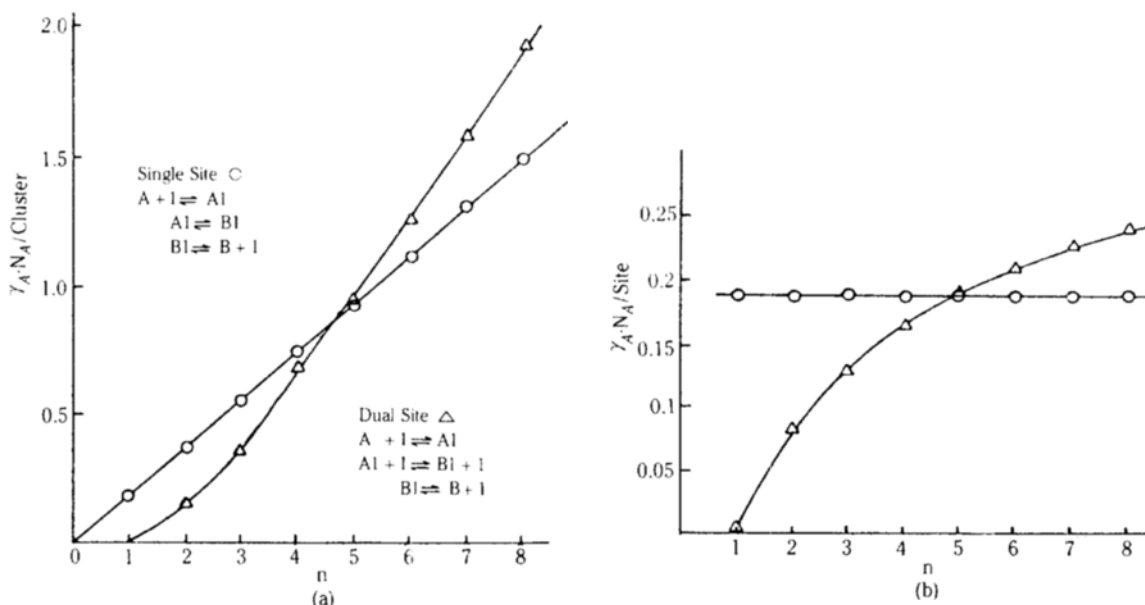

Fig. 1. Reaction rates per (a) cluster and (b) site for single and dual site mechanisms.
(Single site: $\alpha_1 = 2, \alpha_2 = 1$, $\beta_1 = 1$, $\beta_2 = 2$, $\gamma_1 = 1, \gamma_2 = 1$, Dual site: $\alpha_1 = 2, \alpha_2 = 1$, $\beta_1 = 1$, $\beta_2 = 2$, $\gamma_{11} = 1, \gamma_{12} = 1$)

DEACTIVATING CATALYST

The pseudo-steady state assumption also prevails when the rate constants of deactivation reaction (herein ten of η) are taken very small with respect to other rate constants of reactions involved. The set of differential equations derived from eqn. (3) for each combination is solved by Runge-Kutta-Gill method. The number of differential equations describing the

state of the cluster depends entirely on the reaction mechanisms and the cluster sizes. For instance, if the coking reaction follows the mechanism 11, 14,16 and 19 in Table 1, it is impossible that all reaction sites are covered with coke; $P(0,0,0,n) = 0$, since at least one of two sites involved in deactivation reaction can never be covered with coke.

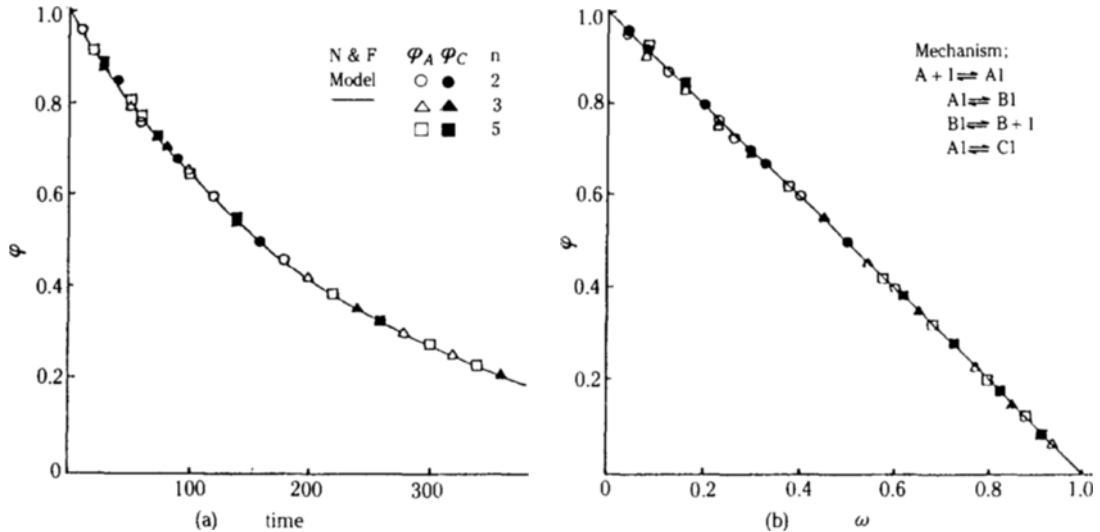As defined in eqns. (10) and (11), the deactivation function and the degree of coverage are also estimated
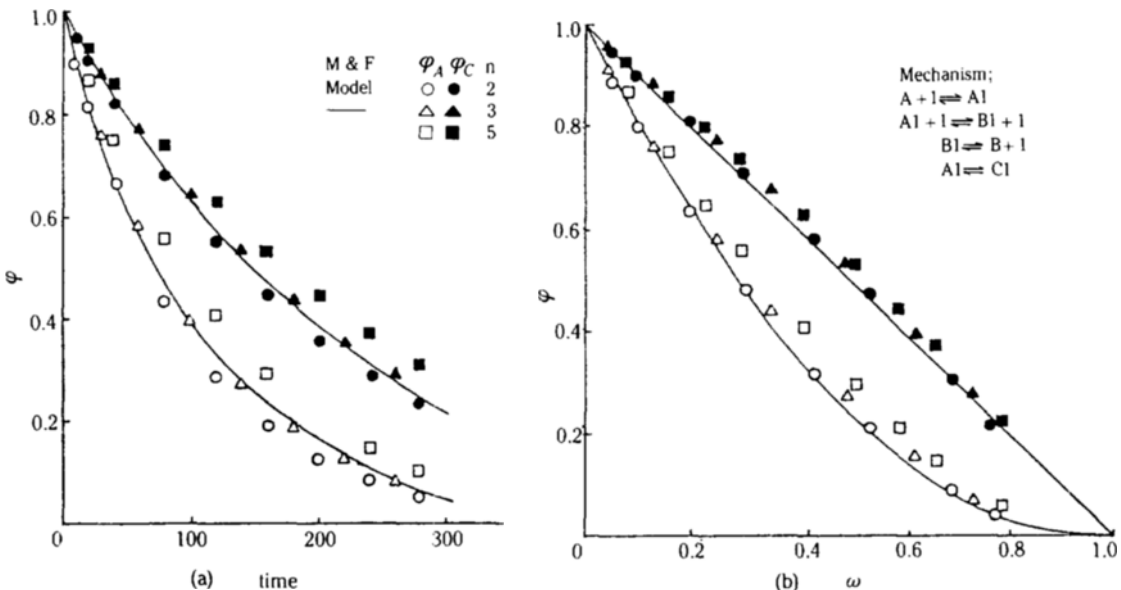

Fig. 2. Dependence of deactivation functions on (a) time and (b) coke coverage for 1-1 reactions.
$(\alpha_1 = 2, \alpha_2 = 1, \beta_1 = 1, \beta_2 = 2, \gamma_1 = 1, \gamma_2 = 1, \eta_1 = 0.01$, rest of parameters $= 0)$

Fig. 3. Dependence of deactivation functions on (a) time and (b) coke coverage for 2-1 reactions.
$(\alpha_1 = 2, \alpha_2 = 1, \beta_1 = 1, \beta_2 = 2, \gamma_{11} = 1, \gamma_{12} = 1, \eta_1 = 0.01$, rest of parameters $= 0)$

by solving the set of differential equations derived from eqn.(3). It is very interesting to compare the deactivation functions calculated from this study with the deactivation function model by Nam and Froment [1]. They developed the exclusive relationships for the deactivation functions and the degree of coverage depending upon the reaction mechanisms for multi-site

reaction without any information of reaction rates.

Figs. 2, 3, 4 and 5 show the consistency of the deactivation functions obtained by both approaches for four cases described in Nam and Froment [1]; this study is designated by symbols and Nam and Froment's model [1] by solid lines. The simulation was made for the first mechanism of each reaction system shown in
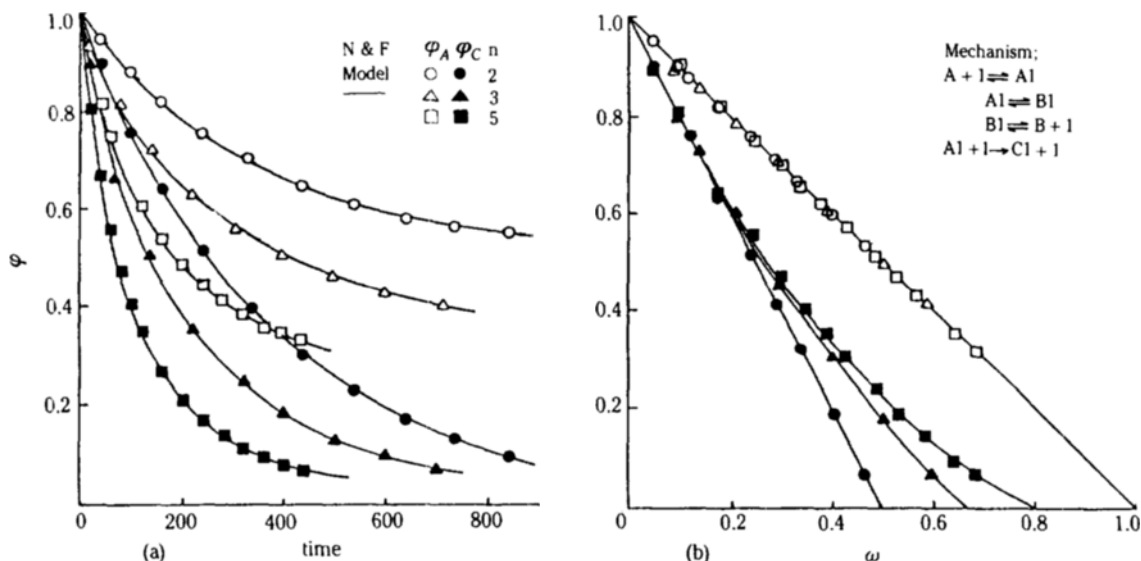

Fig. 4. Dependence of deactivation functions on (a) time and (b) coke coverage for 1-2 reactions.
($\alpha_1 = 2$, $\alpha_2 = 1$, $\beta_1 = 1$, $\beta_2 = 2$, $\gamma_1 = 1$, $\gamma_2 = 1$, $\eta_{11} = 0.01$, rest of parameters = 0)
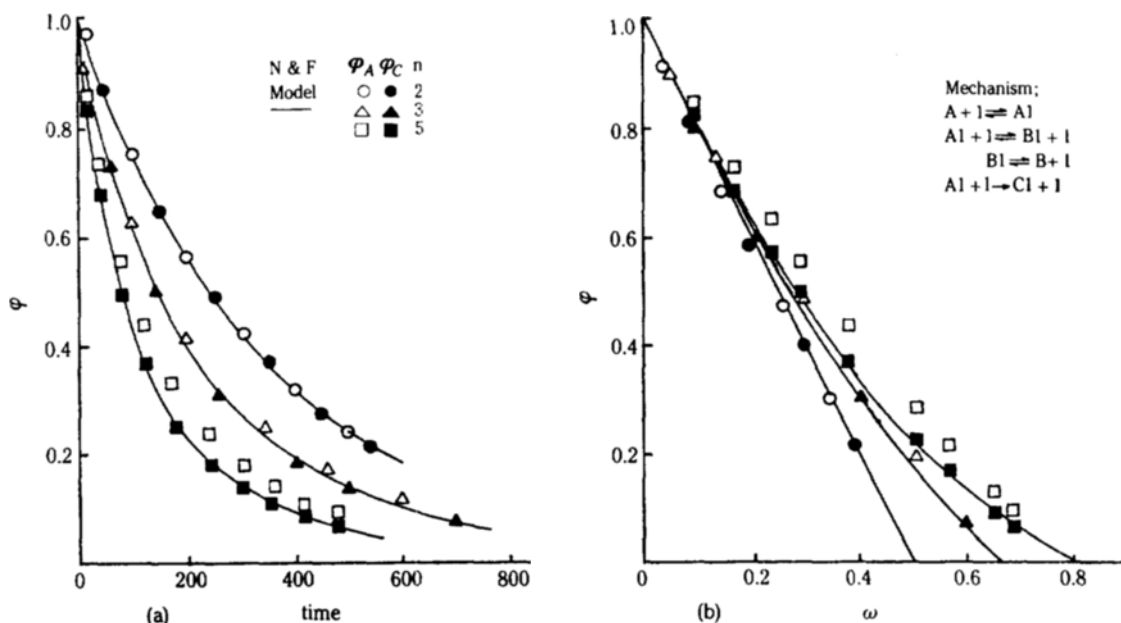

Fig. 5. Dependence of deactivation functions on (a) time and (b) coke coverage for 2-2 reaction.
($\alpha_1 = 2$, $\alpha_2 = 1$, $\beta_1 = 1$, $\beta_2 = 2$, $\gamma_{11} = 1$, $\gamma_{12} = 1$, $\eta_{11} = 0.01$, rest of parameters = 0)

Table 2 with $\eta = 10^{-2}$. The rest of parameters are given in the relevant figures. Again the pseudo-steady state assumption is confirmed by the comparison of three reaction rates shown in eqns. (4), (5) and (6) for each time interval. As extensively discussed by Nam and Froment [1], catalyst with higher dispersion (smaller cluster size in this study) is more resistant to deactivation than catalyst with low dispersion when the coking reaction occurs on the dual site shown in Figs. 4(a) and 5(a). These are identical to Nam and Froment's result [1] and are also experimentally confirmed by Barbier et al. [7].

Other reaction mechanisms can also be considered to compare with the Nam and Froment's deactivation model. However, the present study requires a lot of effort to solve a set of differential equations which frequently include numerical problem with the pseudo-steady state assumption. But the reaction rates for main and coking reactions can be directly calculated from the present model. On the other hand, Nam and Froment [1] developed exclusive deactivation functions with the degree of coverage without any direct information of the reaction rates.

CONCLUSION

A stochastic method developed in this study is quite general to quantify the state of the reaction sites in the cluster both for fresh and deactivating catalyst. A set of differential equations, e.g. eqn. (3), represents a reaction system specified by the reaction mechanism. The solution of the system of equations gives much information on the reaction kinetics. Particularly, the deactivation functions and the degree of coverage calculated from this study are well represented by the model developed by Nam and Froment [1]. It indicates that the present approach is quite useful to describe the catalyst deactivation by site coverage. Note that the size of parameters for the simulation is quite insensitive to the final results of this study shown in Figs. 1, 2, 3, 4 and 5.

Furthermore, it is observed that the dual site main reaction belongs to the class of structure-sensitive reaction in terms of reaction sites for the fresh catalyst. However, for the deactivation catalyst, the rates of deactivation functions become structure sensitive regardless of the reaction mechanism when the coking reaction occurs on the dual site, while the rates of the deactivation functions with single site coking reaction is structure-insensitive independent of the reaction mechanism. It indicates that the mechanism of coking reaction is critical for the reaction classification by Boudart [8].

Although the present approach requires a lot of computing time to solve the set of differential equations as many as 56 for n = 5, this approach is quite fundamental to the examination of the reaction kinetics in association with the physical properties of catalyst such as the cluster size. The extension of this approach to the any reaction mechanisms and any number of sites can be made.

ACKNOWLEDGEMENT

NOMENCLATURE

A,B,C	:	reactant, product and coke, respectively
i	:	number of free sites in a cluster
j	:	number of sites reversibly adsorbed by A
k	:	number of sites reversibly adsorbed by B
l	:	reaction site
m	:	number of sites irreversibly covered by coke
n	:	total number of sites in a cluster
t	:	process time, arbitrary unit
$\alpha, \beta, \gamma, \eta$	:	conditional probability per unit time provided the transition from active to non-viable state
φ_A	:	deactivation function for main reaction
φ_C	:	deactivation function for coking reaction
ω	:	degree of site coverage

REFERENCES

1. Nam, In-Sik and Froment, G.F.: *J. of Catal.*, **108**, 271 (1987).
2. Hougen, O.A. and Watson, K.M.: "Chemical Process Principle, Part III", John Wiley & Sons, Inc., (1954).
3. Froment, G.F.: Proc. Int. Cong. Catal. 6th, London, 10 (1976).
4. Herrington, E.F.G. and Rideal, E.K.: *Trans. Far. Coc.*, **40**, 505 (1944).
5. Welsch, R.J. and Butt, J.B.: *Chem. Eng. Commun.*, **1**, 155 (1973).
6. Fredrickson, A.G.: *Chem. Eng. Sci.*, **1**, 687 (1966).
7. Barbier, J., Corro, G., Zhang, Y., Bournonville, J.P., and Franck, J.P.: *Applied Catalysis*, **13**, 245 (1985).
8. Boudart, M.: Proc. Int. Congr. Catal. 6th, London, 1 (1976).