JOURNAL OF CATALYSIS **91,** 254–262 (1985)

Kinetics and Mechanism of Deactivation of Pd–Al_2O_3 Catalyst in the Gaseous Phase Decarbonylation of Furfural

R. D. SRIVASTAVA AND A. K. GUHA

Department of Chemical Engineering, Indian Institute of Technology, Kanpur-208016, India

Received December 1, 1983; revised August 16, 1984

The kinetics of decarbonylation of furfural to furan as well as the kinetics and mechanism of deactivation by coking of Pd–Al_2O_3 catalyst have been examined. A statistically best-rate expression for the main reaction, developed on the basis of the surface reaction on two active sites, was determined from the experimental data. Deactivation occurred in parallel with the main reaction. The deactivation kinetic equation was governed by the reaction of two adjacent adsorbed furfural molecules resulting in the coke precursor. © 1985 Academic Press, Inc.

INTRODUCTION

Catalyst deactivation and regeneration are important and form the major fields of catalysis. Among the various possible reasons for deactivation, the most common is the deposition of carbon which blocks the active surface. This may be due to side reactions or to decomposition of the organic reactant. As a consequence, the kinetic study of the main reaction in itself becomes seriously complicated.

In spite of several studies made of the kinetics of deactivation processes, there is still no generalized approach to analyze this problem because of the wide variation in the chemical aspects of coke formation (*1, 2*). Earlier studies contemplated the catalyst activity as dependent only on the reaction time which revealed very little information about the mechanism of deactivation as summarized in Ref. (*2*). Further studies on deactivation of catalyst particles under diffusional control (*3, 4*) and in fixed-bed reactors (*5, 6*) have demonstrated that the deactivation also depended upon the reaction conditions.

It is generally accepted that the rate of main reaction in presence of coking can be expressed as

$$(-r_A) = (-r_A)_0 \cdot a, \qquad (1)$$

where a is termed as "activity" (*7*). Some authors prefer to use ϕ_A (*8*) or Ψ_A (*9*) as a deactivation function for activity. The kinetic equation of the main reaction is given by $(-r_A)_0$ and is determined by using kinetic data at zero coke content. It is obvious that some relationship which gives the value of the activity during reaction is required along with Eq. (1). It is at this point where the controversies still exist.

Froment and co-workers (*10–12*) developed a complex technique to relate the activity to the coke content through an empirical equation. The coke content of the catalyst was then related to the composition of the reaction mixture, temperature, and time, through a continuity equation for coke which needs integral reactor together with thermo-balance data of the deposited amount of coke. On the other hand, Szepe and Levenspiel (*7*), Levenspiel (*13*), Wolf and Petersen (*14–17*), Corella *et al.* (*18*), and Corella and Asua (*19*) prefer to relate the activity to the reaction conditions directly. The analysis with the use of single-pellet diffusion reactor (*14–17*) requires an accurate measurement of "center plane concentration."

0021-9517/85 $3.00

Szepe and Levenspiel (*7*) used an equation with separable variables for the deactivation of the form

$$-\frac{da}{dt} = f_1(T) \cdot f_2(C_i) \cdot f_3(\mathrm{a}). \qquad (2)$$

The overall chemical reaction rate expression consisted of a reaction-rate function multiplied by a deactivation function as

$$(-r_\mathrm{A}) = f_4(T) \cdot f_5(C_i) \cdot a. \qquad (3)$$

Thus by keeping the reaction mixture composition and the temperature constant, the variation in the rate of reaction due solely to the deactivation process can be studied directly. It should be noted that their method of analysis of experimental data is valid only in the case where concentration dependency function is previously evaluated on the basis of experiments and which are generally of power-law type.

The above method of analysis was later extended by several authors (*12, 14, 15, 18–21*) to the point where the kinetics of the main reaction was of the Hougen–Watson type or at which the variables were nonseparable

$$-\frac{da}{dt} = \Psi(p_i,T) \cdot f_3(a), \qquad (4)$$

where $\Psi(p_i,T)$ is the deactivation function.

Corella and Asua (*22*) generalized theoretically the kinetics of deactivation by coking where Eq. (4) was accomplished and obtained the equation

$$-\frac{da}{dt} = \Psi(p_i,T) \cdot a^d, \qquad (5)$$

where $d = (m + h - 1)/m$, m and h are the number of active sites involved in the controlling step of the main reaction and the deactivation reaction, respectively. This is a more fundamental approach to the analysis of catalyst deactivation.

The present work is an utilization of the above method to a catalytic reaction system of interest for industrial applications and scientific research, the decarbonylation of furfural to furan over Pd–Al_2O_3 catalyst (*23–24*). A careful examination of the literature revealed that there is no prior deactivation kinetic study for this catalytic reaction system. The experimental results are analyzed on the basis of Langmuir–Hinshelwood kinetics for the main reaction as well as for the deactivation, with statistical data interpretation to show the real significance of mechanism determination with precise experimental data. It is expected that the present results will contribute to the understanding of the deactivation kinetics of such catalytic systems.

EXPERIMENTAL

Catalyst was tested primarily for initial activity and resistance to deactivation using a micropulse reactor–chromatograph assembly, Hewlett–Packard Model 5880. With this apparatus either single pulse or a train of pulses of known volume of furfural and frequency can be automatically passed through the catalyst bed (1 cm length, 0.3 cm diameter, containing 0.2–0.3 gm crushed catalyst of 0.1 mm mean diameter), using a suitable carrier such as N_2 or H_2. Furfural pulse rate was 1 μl/sec. The flow rate of carrier gas was 30 ml/min. The temperature was varied from 450 to 600°K, and was controlled to within 1°C.

Preliminary experiments demonstrated that the catalyst lost its activity rapidly in the absence of hydrogen and that part of this lost activity could be recovered by increasing the hydrogen pressure during the reaction. The micropulse reactor enabled a promising operating conditions to be quickly found. Catalyst was then readily tested in a larger scale reactor to obtain kinetic data.

The fixed-bed reactor with general experimental procedure was similar to that described in Ref. (*25*). The furfural was fed by the calibrated metering pump into a preheater, where it was mixed with N_2 gas and vaporized. The vapor was then led to the reactor containing the catalyst bed. The temperature of the catalyst bed was mea-

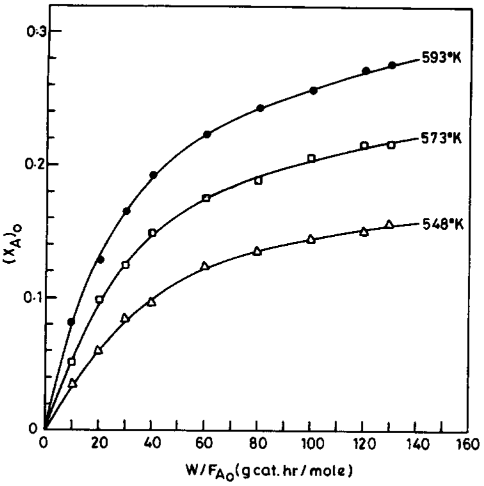


FIG. 1. Conversion at time zero against space time.

sured by an iron–constantan thermocouple located in a coaxial thermowell. The main stream of the effluents from the reactor was cooled by a set of condensers. The liquid condensate was analyzed by GLC and the gaseous products were metered. A stainless-steel tube packed with 10% Carbowax-20M on Chromosorb W was used as analyzing column in the chromatograph. The sole product of decarbonylation of furfural was furan on Pd–Al_2O_3. All experiments described below were performed exclusively with 5% Pd on Al_2O_3, 3-mm spherical pellets (Houndry Chemicals).

The effects of diffusion were kept to a minimum by passing the gas at high velocity through the catalyst. The fair constancy of conversion obtained by changing the feed rate while keeping (W/F) constant suggested that the diffusion of gases was not controlling the rate. The role of internal diffusion was checked by varying the size of the catalyst particles while maintaining the catalyst weight, $\bar{R}$, and (W/F) constant. The internal diffusion resistance in the catalyst particles was practically negligible as observed by the insignificant change in the reaction rate. To study the effect of external diffusion, it was necessary to increase the bed height while keeping ($\bar{R}$) and (W/F) constant. The rate was unaffected by doubling the bed height. Thus the external diffusion in the catalyst bed was negligible. Rate calculations were based on conversion to furan.

RESULTS AND DISCUSSION

Kinetic Equation at Operation Time Zero

The kinetics of the main reaction were studied in an integral reactor by using data at zero coke content. These set of experiments lasted 4 hr and were conducted with the following operating conditions:

$$\bar{R}\left(\frac{\text{moles of furfural}}{\text{moles of nitrogen}}\right) = 2,$$

temperature range 548–593°K

W/F_{A0}(g-cat. hr/mole) = 10–130.

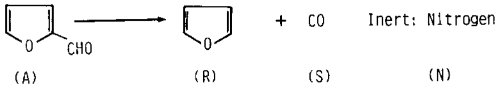
Figure 1 shows the conversion data at time zero against space time for all the temperatures under consideration. The values of rate of reaction at zero time $(-r_A)_0$ were obtained by second-order polynomial adjustment of the curves $(X_A)_0$ vs W/F_{A0} followed by analytical differentiation. These data have been analyzed according to the method discussed by Froment and Hosten (*26*). The techniques of linear and nonlinear estimates were applied to various mathematical rate expressions as a method of correlating the experimental data. Different models based on Langmuir–Hinshelwood mechanisms were formulated.

Mathematical Modeling Technique

A nonlinear regression algorithm (*25*) utilizing Marquardt's algorithm (*27, 28*) was used to obtain a mathematical fit for various rate expressions. The program minimized the residual sum of squares (R.S.S.) during the regression. The nonlinear computer program basically improved upon the initial estimates of various constants of the rate equation until the R.S.S. could no longer be reduced. Approximate 95% confidence intervals for various constants were calculated from estimates of their individual variances. The starting values of the parameters were estimated by linear regression.

Once the model satisfied the criterion of parameter values to be physically significant, then the goodness of fit of the model was checked by performing an F-test.

The decarbonylation of furfural to furan may be represented as



(6)

Thermodynamic calculations have shown that the reaction is essentially irreversible ($\ln K > 13$, temperatures 523–623°K). The method of Yang and Hougen (*29*) was used to eliminate some of the rate-controlling steps. The rate data showed that the desorption of product was not a rate-controlling step.

The Langmuir–Hinshelwood isothermal rate equation based on single- and dual-site mechanisms for the reaction were considered. These rate equations were derived with an adsorption term for each of the reaction components and diluent nitrogen. The regressions of the rate equations were made at each temperature. The isothermal rate equations, basic type of which are given in Table A-1 of the Appendix, resulted in 8 different mathematical forms, which were confronted with the experimental data. Since the experiments were limited to pure feed, containing only A as reacting component, the stoichiometry ($p_R = p_s$) did not permit us to calculate parameters K_R and K_s individually and they have been coupled as K_{RS}.

The data were most satisfactorily correlated by the model

$$(-r_A)_0 = \frac{kK_Ap_A}{(1 + K_Ap_A + K_{RS}p_R)^2}, \qquad (7)$$

where surface reaction on two active sites is the rate controlling. The values of kinetic constants k, K_A, and K_{RS} are shown in Table 1.

An F-test was made on the residual for this model, in which six replicates were carried out. The F_{observed}-value of 2.1 lie within the range $0 \leq F_{\text{observed}} \leq F(13,15,0.95) = 2.5$.

TABLE 1

Values of the Kinetic Constants

T (°K)	k	K_A	K_{RS}
548	$(18.7 \pm 2.5) \times 10^{-3}$	2.8 ± 1.7	39.9 ± 15.1
573	$(35.7 \pm 5.7) \times 10^{-3}$	0.5 ± 0.24	12.5 ± 5.6
593	$(68.6 \pm 11.7) \times 10^{-3}$	0.28 ± 0.14	8.5 ± 4.5

The following relation between the kinetic constants and the temperature has been determined

$$k = 16{,}751 \exp(-7448/T) \qquad (8)$$

$$K_A = 1.4 \times 10^{-13} \exp(16{,}685/T) \qquad (9)$$

$$K_{RS} = 6.5 \times 10^{-9} \exp(12{,}349/T). \qquad (10)$$

The activation energy for the main reaction is calculated as 62 kJ/mole.

Kinetics of Deactivation

In order to determine whether the deactivation is in parallel or in series with the main reaction, preliminary experiments were performed with 10% furan in the feed at 573°K. The results showed that addition of furan had no appreciable effect on the reaction rate. These experiments gave some indication for parallel deactivation, however, it was further supported by performing a series of experiments in a differential reactor for a series of $\overline{R}$ at 573°K and $W/F_{A0} = 15$. Activity, a', was calculated as quotient between conversion at time t and at zero time.

The composition of the reacting mixture is constant throughout the reactor in a differential reactor. Therefore, Eq. (5) can be integrated for $h \neq 1$ as

$$(a'^{(1-h)/m} - 1) = (h - 1)\Psi_0(p_{i0},T) \cdot t. \qquad (11)$$

The slope of the straight line, obtained from the plot of $(a'^{(1-h)/m} - 1)/(h - 1)$ against time is the deactivation function $\Psi_0(p_{i0},T)$ (*18*).

Figure 2 shows a plot of $(a'^{(1-h)/m} - 1)/(h$

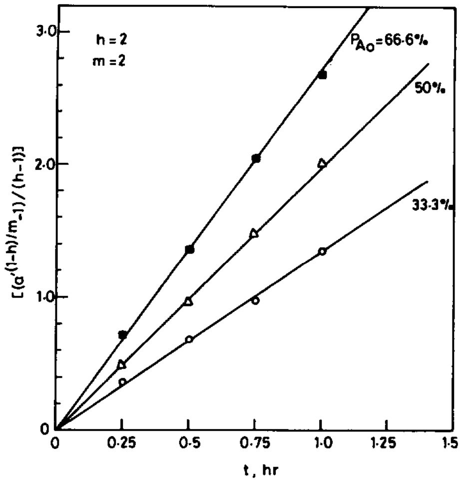


FIG. 2. Plot $(a'^{(1-h)/m} - 1)/(h - 1)$ vs time for differential reactor at 575°K.

$- 1)$ vs time for $h = 2$ and $m = 2$. The calculated $\Psi_0(p_{i0},T)$ values for a series of average partial pressures of furfural are listed in Table 2.

An increase in $\Psi_0(p_{i0},T)$ values with p_{A0} suggests the deactivation to be parallel (*18, 22*), in agreement with the ones obtained from the preliminary experiments.

Accordingly, the reaction scheme with deactivation may be represented as

$$\begin{aligned} &A \rightarrow R + S \\ &A \rightarrow \text{Coke}. \end{aligned} \qquad (12)$$

To evaluate the kinetic equation of deactivation, the deactivation data from experiments carried out in an integral reactor are shown in Fig. 3.

The reaction rates are obtained by polynomial adjustment (second order) of the curves X_A vs W/F_{A0} followed by analytical differentiation. The values of the rate of reaction $(-r_A)$ for different times together with the rate of reaction at time zero were obtained for $W/F_{A0} = 60$. With these values for $(-r_A)$ and $(-r_A)_0$ corresponding activity values have been calculated for each value of the partial pressure of the reactant conforming to Eq. (1) and plotted against time in Fig. 4. The deactivation rate $(-da/dt)$ is

TABLE 2

$\Psi_0(p_{i0},T)$ Experimental Values for Different p_{A0}

	$\bar{R}$		
	0.5	1	2
p_{A0}	0.33	0.50	0.66
$\Psi_0(p_{i0},T)$	1.34	1.98	2.71

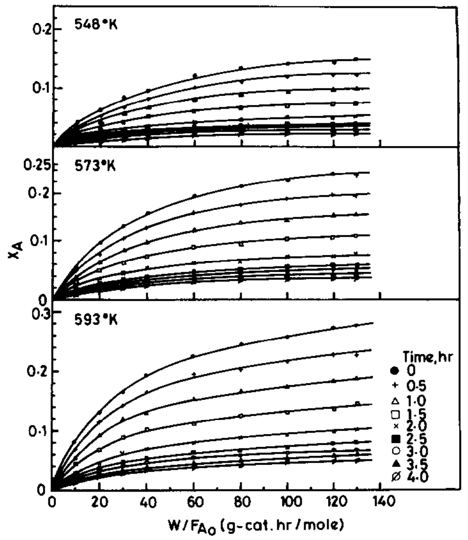


FIG. 3. Conversion against space time for different process times at the temperatures 548, 573, and 593°K.

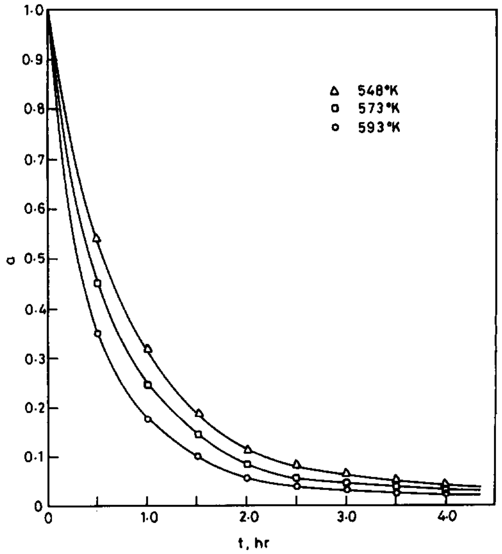


FIG. 4. Activity against process time.

TABLE 3

Deactivation Function Values

t (hr)	p_A (atm)	p_R (atm)	$\Psi(p_A,T)$	
			$h = 1$	$h = 2$
Temperature: 593°K				
0.0	0.447	0.131	2.337	2.337
0.5	0.480	0.111	1.483	2.527
1.0	0.514	0.091	1.145	2.725
1.5	0.549	0.070	0.926	2.926
2.0	0.583	0.049	0.747	3.124
2.5	0.602	0.038	0.642	3.233
3.0	0.612	0.032	0.590	3.292
3.5	0.620	0.027	0.540	3.338
4.0	0.628	0.022	0.489	3.384
Temperature: 573°K				
0.0	0.491	0.105	1.976	1.976
0.5	0.518	0.088	1.407	2.097
1.0	0.546	0.072	1.104	2.222
1.5	0.574	0.055	0.888	2.349
2.0	0.601	0.039	0.714	2.472
2.5	0.616	0.030	0.606	2.539
3.0	0.624	0.025	0.559	2.575
3.5	0.630	0.021	0.507	2.604
4.0	0.637	0.017	0.460	2.632
Temperature: 548°K				
0.0	0.542	0.074	1.523	1.523
0.5	0.561	0.063	1.167	1.593
1.0	0.581	0.050	0.936	1.665
1.5	0.602	0.038	0.756	1.738
2.0	0.621	0.027	0.607	1.807
2.5	0.631	0.020	0.513	1.845
3.0	0.637	0.017	0.473	1.865
3.5	0.641	0.014	0.429	1.881
4.0	0.646	0.012	0.388	1.897

evaluated by derivation of these curves. The deactivation function, $\Psi(p_A,T)$, calculated from

$$\Psi(p_A,T) = (-da/dt)/a^{(m+h-1)/m} \qquad (13)$$

are listed in Table 3.

The possible isothermal deactivation rate equations based on single- and dual-site mechanisms for the reaction (12), which assume that the rate-controlling step was the coke precursor formation (second step), are presented in Table A-2 of Appendix. To evaluate the parameters of the deactivation rate equation, the values of K_A and K_{RS} of the main reaction have been used and the same nonlinear regression technique was employed.

The model which correlated with the data most satisfactorily is

$$-\frac{da}{dt} = \frac{k_d K_{A^*}^2 p_A^2}{(1 + K_A p_A + K_{RS} p_R + K_{A^*} p_A)^2} \cdot a^{1.5}. \qquad (14)$$

This model was based on the mechanism that two adjacent adsorbed furfural molecules are involved in the formation of coke precursor $P_1 l_2$, ultimately leading to coke lay down according to the scheme

$$A + l \rightleftharpoons A^*l \qquad (15)$$

$$A^*l + A^*l \rightarrow P_1 l_2 \rightleftharpoons P_2 l_2 \rightleftharpoons P_3 l_2 \ . \ . \ . \ \text{Coke} \qquad (16)$$

where the coke precursor formation step is found to be rate controlling and the furfural adsorbed in a way different from the main reaction. The same phenomena has been reported by Tamura (*30*) in the catalyst deactivation during ethylene hydrocyanation in gaseous phase and by Jodra *et al.* (*20*) in the dehydrogenation of benzyl alcohol over a Cu–Cr$_2$O$_3$/asbestos catalyst, the benzyl alcohol was adsorbed in different ways in the main reaction and in the deactivation reaction.

The parameter values corresponding to the Eq. (14) are listed in Table 4.

The relation between the constants of deactivation equation and the temperature is given by the equations

$$k_d = 1315 \exp(-3392/T) \qquad (17)$$

$$K_{A^*} = 4.4 \times 10^{-4} \exp(6092/T). \qquad (18)$$

TABLE 4

Kinetic Constants for the Deactivation Reaction

T (°K)	k_d	K_{A^*}
548	2.4 ± 0.005	38.3 ± 0.001
573	3.5 ± 0.003	15.5 ± 0.002
593	4.7 ± 0.007	11.7 ± 0.004

The activation energy for deactivation reaction is 28 kJ/mole which is less than that of the main reaction, indicating the deactivation reaction rate is less sensitive to temperature to that of the main rate of reaction. The low value of activation energy is generally indicative of reversible deactivation reaction (*17*). The high value of K_{A^*} indicates a strong adsorption of A on the catalyst surface which will produce a fast deactivation when particles with diffusional limitations are used.

CONCLUSIONS

Rate equation for the decarbonylation of furfural to furan along with the kinetics and mechanism of deactivation of Pd–Al_2O_3 catalyst have been determined. For the decarbonylation, the kinetics can be described by assuming the rate-determining step is the two-site decarbonylation of the furfural. The rate of deactivation which occurs by parallel mechanism is presumed to be controlled by the reaction between two adsorbed furfural to form coke precursor followed by coking sequence ultimately leading to the formation of coke. The derived rate equation represents the data satisfactorily when all sites are taken as identical and furfural adsorbed in a different way than the main reaction. Thus, the initial rate equation, deactivation rate equation, and relation between initial rate and rate at any time can be treated simultaneously to describe the kinetics of the catalytic reaction system completely.

The present results have provided further experimental test of the method of analysis recently proposed by Corella and Asua. It is expected that their approach will contribute significantly to the understanding of kinetics and mechanism of catalyst deactivation since it relates activity directly to the deactivation reaction.

APPENDIX 1: NOMENCLATURE

A,R,S,N	furfural, furan, carbon monoxide, and nitrogen, respectively
Al	furfural adsorbed in the main reaction
A*l	furfural adsorbed in different way than in the main reaction
a	catalyst activity, integral reactor
a'	catalyst activity, differential reactor
C_i	concentration of i
d	deactivation order
F_{A0}	feed rate of furfural, mole/hr
h	number of active sites involved in the controlling step of deactivation reaction
K_A,K_R,K_S,K_N	equilibrium adsorption constants for furfural, furan, carbon monoxide, and nitrogen, respectively in the main reaction, atm
K_{RS}	sum of K_R and K_S, atm
K_{A^*}	equilibrium adsorption constant for furfural to yield coke precursor, atm
k	rate constant of the main reaction, mole/g-cat. hr
k_d	rate constant of the deactivation reaction, hr^{-1}
l	active site
m	number of active sites involved in the controlling step of the main reaction
n	number of molecules of A in gas phase which react with the adsorbed A to give the coke precursor
P_1l_2,P_1l_h	coke precursor
$P_2l_2,P_3l_2,$ P_2l_h,P_3l_h	different forms of coke in the coking sequence
p_A,p_R,p_S,p_N	partial pressures of furfural, furan, carbon monoxide and nitrogen, respectively, atm
p_i	partial pressure of i
p_{A0}	partial pressure of furfural at the reactor entrance, atm

$\bar{R}$	mole ratio of furfural to nitrogen
$(-r_A)$	rate of reaction of A, mole/g-cat. hr
$(-r_A)_0$	rate of reaction of A at zero time
$(-\bar{r}_A)$	calculated rate of reaction of A
T	absolute temperature, °K
t	time, hr
W	weight of catalyst in reactor, g
X_A	conversion of furfural at any time
$(X_A)_0$	conversion of furfural at zero time

Greek Letters

$\Psi(p_i,T)$	deactivation function
$\Psi(p_A,T)$	deactivation function, integral reactor
$\Psi_0(p_{i0},T)$	deactivation function, differential reactor

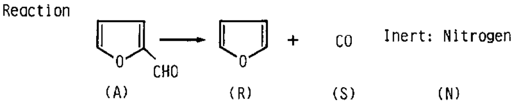
Definitions

$$\text{R.S.S.} = \sum_{j=1}^{i} (\bar{r}_A(j) - r_A(j))^2$$

APPENDIX 2: RATE EQUATIONS

TABLE A-1

Isothermal Rate Equations



A. Single-site mechanism

Rate-controlling step	Rate equation
a. Adsorption of furfural (A)	$kK_Ap_A/(1 + K_Rp_R + K_Sp_S + K_Np_N)$
b. Surface reaction	$kK_Ap_A/(1 + K_Ap_A + K_Rp_R + K_Sp_S + K_Np_N)$

B. Dual-site mechanism

Rate-controlling step	Rate equation
a. Adsorption of furfural (A)	$kK_Ap_A/(1 + K_Rp_R + K_Sp_S + K_Np_N)$
b. Surface reaction	$kK_Ap_A/(1 + K_Ap_A + K_Rp_R + K_Sp_S + K_Np_N)^2$

TABLE A-2

Isothermal Deactivation Rate Equations Assuming Step 2 as Rate Controlling

d-1 Mechanism

Step 1 $A + l \rightleftharpoons Al$
Step 2 $nA(g) + hAl \rightarrow P_1l_h$
Step 3 $(P_1l_h) \rightleftharpoons (P_2l_h) \rightleftharpoons (P_3l_h)$ . . . Coke

m	*h*	*n*	Model equation
2	1	0	$-\frac{da}{dt} = \frac{k_dK_Ap_A}{1 + K_Ap_A + K_{RS}p_R} \cdot a$
2	1	1	$-\frac{da}{dt} = \frac{k_dK_Ap_A^2}{1 + K_Ap_A + K_{RS}p_R} \cdot a$
2	2	0	$-\frac{da}{dt} = \frac{k_dK_A^2p_A^2}{(1 + K_Ap_A + K_{RS}p_R)^2} \cdot a^{1.5}$

d-2 Mechanism

Step 1 $A + l \rightleftharpoons A^*l$
Step 2 $nA(g) + hA^*l \rightarrow P_1l_h$
Step 3 $(P_1l_h) \rightleftharpoons (P_2l_h) \rightleftharpoons (P_3l_h)$ . . . Coke

m	*h*	*n*	Model equation
2	1	0	$-\frac{da}{dt} = \frac{k_dK_{A^*}p_A}{1 + K_Ap_A + K_{RS}p_R + K_{A^*}p_A} \cdot a$
2	1	1	$-\frac{da}{dt} = \frac{k_dK_{A^*}p_A^2}{1 + K_Ap_A + K_{RS}p_R + K_{A^*}p_A} \cdot a$
2	2	0	$-\frac{da}{dt} = \frac{k_dK_{A^*}^2p_A^2}{(1 + K_Ap_A + K_{RS}p_R + K_{A^*}p_A)^2} \cdot a^{1.5}$

ACKNOWLEDGMENT

Dr. P. N. Tewari is gratefully acknowledged for experimental assistance.

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