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Cumene Cracking on a Diffusion-Limited Aging Catalyst

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The Campbell-Wojciechowski mechanism of cumene cracking is applied to conversion data obtained using a series of LaY zeolite catalysts of various particle sizes. A study of the parameters obtained by fitting the model to data for each particle size allows a qualitative interpretation of the effects of intraparticle diffusion in an aging catalyst to be made.

As a result of such considerations a new test to evaluate the significance of intraparticle diffusion in this reaction is introduced. Using this test it is shown that LaY catalyst particles as small as 70/80 mesh are diffusion limited for cumene cracking. Nonetheless, the activation energy for the cracking reaction using the diffusion limited 70/80 mesh catalyst was found to be 22.1 kcal/mole, in disconcertingly good agreement with previously reported values.

It is also shown that if site poisoning proceeds by the dimerization of adsorbed species cumene, not propylene as previously suspected, is the probable poisoning agent in the cumene cracking reaction. At the same time "coke on catalyst" is shown not to be directly related to catalyst activity.

NOMENCLATURE

B	Benzene
C	Cumene
CS	Adsorbed cumene
E_2	Activation energy of k_2
E_c	Energy of adsorption of C
ΔE	Energy of reaction
G	Aging constant, sec^{-1}
$[P]$	Concentration of poison, atm
K	Adsorption equilibrium constant, atm^{-1}
N	Aging exponent, dimensionless
P	Catalyst/reagent ratio (weight ratio)
[S]	Concentration of active sites at t, sites/m^2
[S_0]	Initial concentration of actives sites, sites/m^2
T	Temperature, K
Y, Z	Products (propylene and benzene)
YS	Adsorbed product
τ	Space time, sec
[ ]	Concentration, atm
b	Proportionality constant
k_d	Deactivation rate constant
m	Number of sites involved in a deactivating event
n	The order of a catalytic reaction with respect to the concentration of active sites
p, q, s	Model parameters
p', q', s'	Modified model parameters, sec
V_r	Rate of disappearance of cumene, atm/sec
t	Time-on-stream, sec
x	Instantaneous fractional conversion
$\bar{x}$	Integral fractional conversion

Subscripts

0	Initial conditions
f	Final conditions
e	Equilibrium
c, y, z	Component C, Y, Z.

INTRODUCTION

Cumene cracking has long been considered an attractive reaction to use as a standard test to characterize acid cracking catalysts (*1*). Consequently, many studies of this reaction have appeared in the literature and these have been recently reviewed by Rabo and Poutsma (*2*), by Minachev (*3*) and by Venuto (4).

The behavior of the reaction has been studied both kinetically and spectroscopically (*2*, *6*, *7*). On the evidence available from studies to date, a comprehensive mechanism has been proposed by Campbell and Wojciechowski (*5*). Their mechanism is consistent with other mechanisms in the literature but unlike previous studies, it describes cumene cracking at all levels of conversion and accounts for the aging of the catalyst.

This paper reports work on a series of catalysts each of a different particle size and follows up on previously published work (*5*, *8*) using the same cumene cracking model. Here the model is used to interpret intraparticle diffusion limitations and to study its effects on the reaction parameters. Although diffusion and aging are potentially very important in cracking reactions, little has been done to study both phenomena together. When the Campbell–Wojciechowski cumene cracking model is applied to data obtained at varying degrees of diffusion limitations, an analysis of the parameters obtained allows the effect of intraparticle diffusion on the reaction rate to be separated from aging effects and hence each effect can be studied independently.

In a previous publication (*5*) the cumene cracking mechanism was presented in detail. It is thought that the reaction is initiated by the chemisorption of a cumene molecule on a single active site. This is followed by the removal of the alkyl group via a carbonium ion leaving either benzene or propylene adsorbed on the site. The reverse alkylation reaction is also possible and occurs by a Rideal mechanism. The complete mechanism, termed the delta mechanism, is illustrated in Fig. 1. The delta mechanism is complete in that it includes the adsorption–desorption step for the three major components as well as the reversible reaction of the chemisorbed cumene.

In the original development, it was assumed that the bond-breaking step, i.e.,

$$\mathrm{CS} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{YS} + \mathrm{Z}$$

was the rate-controlling step. Consequently, the rate of disappearance of cumene is written

$$V_r = k_2[\mathrm{CS}] - k_{-2}[\mathrm{YS}] \cdot [\mathrm{Z}]. \qquad (1)$$

By substituting for [CS] and [YS] in terms of the Langmuir adsorption isotherms, accounting for volume expansion, for thermodynamic equilibrium and for aging, the resulting expression for the reaction rate was shown to be (*5*)

$$V_r = \frac{k_2[\mathrm{S}]K_1[\mathrm{C_0}]}{x_e^2}\left(\frac{x_e^2 - x^2}{px^2 + qx + s}\right), \qquad (2)$$

where $p = K_3[\mathrm{C_0}] + K_4[\mathrm{C_0}] - K_1[\mathrm{C_0}] + 1,$
$q = K_3[\mathrm{C_0}] + K_4[\mathrm{C_0}] + 2,$
$s = K_1[\mathrm{C_0}] + 1.$

For purposes of increasing the generality of the model we will here show the consequences of assuming that adsorption or desorption is the rate controlling step.

(i) *Rate Controlled by Desorption*

The desorption of reaction products is represented in the model as

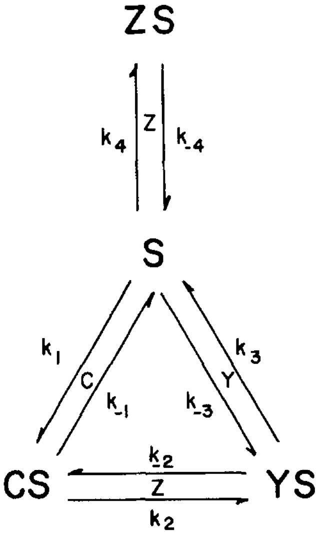

FIG. 1. The delta mechanism for cumene cracking. C represents cumene, S an active site and Y and Z, the products.

$$\mathrm{YS} \underset{k_3}{\overset{k_{-3}}{\rightleftarrows}} \mathrm{Y} + \mathrm{S}.$$

If this step is rate controlling, the rate of the overall reaction is written

$$V_r = k_{-3}[\mathrm{YS}] - k_3[\mathrm{Y}][\mathrm{S}]. \qquad (3)$$

Using the steady state expression [YS] and assuming equilibrium between Z and S, and C and S, we obtain the same expression as that given in Eq. (2) with the parameters p, s, and q now having the meaning given in Table 1.

(ii) *Rate Controlled by Adsorption*

The adsorption of cumene is represented as

$$\mathrm{C} + \mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{CS}.$$

If cumene adsorption is the rate-controlling step, then we can write the rate of reaction as

$$V_r = k_1[\mathrm{CS}][\mathrm{S}] - k_{-1}[\mathrm{CS}].$$

A development analogous to that used in (i) is followed here. Again Eq. (2) results, with the parameters having a new composition as given in Table 1.

When Eq. (2) is combined with the design equation for a plug flow reactor and integrated, the result is

$$\frac{k_2[\mathrm{S}]K_1[\mathrm{C_0}]Pbt_f}{x_e^2} = px + \frac{q}{2}\ln\left(\frac{x_e^2}{x_e^2 - x^2}\right) + \frac{px_e^2 + s}{2x_e}\ln\left(\frac{x_e + x}{x_e - x}\right). \qquad (4)$$

To account for catalyst aging, a decay function of the form shown in equation (5) is used.

$$[\mathrm{S}] = [\mathrm{S_0}](1 + Gt)^{-N}. \qquad (5)$$

The formulation shown in Eq. (5) has been derived from Wojciechowski's time-on-stream theory of catalyst decay (*9*). Substituting (5) into (4) yields the final expression relating instantaneous conversion in a PFR (x), to instantaneous time-on-stream (t).

$$Pbt_f(1 + Gt)^{-N} = p'x + \frac{q'}{2}\ln\left(\frac{x_e^2}{x_e^2 + x^2}\right) + \frac{p'x_e^2 + s'}{2x_e}\ln\left(\frac{x_e - x}{x_e + x}\right),$$

where

$$p' = x_e^2p/k_2[\mathrm{S_0}]K_1[\mathrm{C_0}],$$
$$q' = x_e^2q/k_2[\mathrm{S_0}]K_1[\mathrm{C_0}],$$
$$s' = x_e^2s/k_2[\mathrm{S_0}]K_1[\mathrm{C_0}].$$

The parameters of the model are: G, the aging parameter; N, the aging exponent; and p', s', q', combinations of the rate constants and the adsorption equilibrium constants for the reaction components. The variables of the model are instantaneous conversion x, instantaneous time-on-stream t, final time-on-stream t_f, and the catalyst-to-feed weight ratio P, referred to as the cat/oil ratio. The cumulative conversion $\bar{x}$ is determined using Eq. (7).

$$\bar{x} = \frac{1}{t_f}\int_0^{t_f} x\,dt. \qquad (7)$$

The calculated $\bar{x}$ is compared to the experimental cumene conversion data obtained using a laboratory plug flow reactor.

It is known that when significant resistance to mass transfer exists within a porous particle, a concentration gradient develops. As resistance increases, the concentration of reactant at the interior active sites will decrease until the limiting case is reached of a reaction which consumes reactants much faster than they can be transported to the active site. In this instance, the catalyst on an average sees $[\mathrm{C_0}] \to 0$. This disparity between interior and exterior concentrations can of course be decreased by using smaller catalyst particles. Using this technique of diminishing catalyst particle size intraparticle diffusion effects can be studied.

Examining the parameters p', q', and s' shown in Table 1, it is seen that the rate constant k_2 can be eliminated by using the ratios p'/s' and q'/s'. Remembering also that with increasing mass transfer resistance $[\mathrm{C_0}] \to 0$ in most of the catalyst particle, we note that as the catalyst becomes larger,

$$\frac{p'}{s'} = \frac{K_3[\mathrm{C_0}] + K_4[\mathrm{C_0}] - K_1[\mathrm{C_0}] + 1}{K_1[\mathrm{C_0}] + 1} \to 1,$$
$$\frac{q'}{s'} = \frac{K_3[\mathrm{C_0}] + K_4[\mathrm{C_0}] + 2}{K_1[\mathrm{C_0}] + 1} \to 2, \qquad (8)$$

TABLE 1

RATE EQUATIONS AND MODEL PARAMETERS FOR THREE RATE CONTROLLING STEPS FOR THE CUMENE CRACKING REACTION

	I (Adsorption)	II (Bond breaking)	III (Desorption)
Rate equation	$V_r = \frac{k_2K_1[\mathrm{S}][\mathrm{C}_0](x_e^2 - x^2)}{x_e^2(px^2 + qx + s)}$	$V_r = \frac{k_2K_1[\mathrm{S}][\mathrm{C}_0](x_e^2 - x^2)}{x_e^2(px^2 + qx + s)}$	$V_r = \frac{k_2K_1[\mathrm{S}][\mathrm{C}_0](x_e^2 - x^2)}{x_e^2(px^2 + qx + s)}$
Parameters			
P	$K_3\mathrm{C}_0 + K_AK_3K_2K_1\mathrm{C}_0 + K_4\mathrm{C}_0$ $+ K_1K_2K_4K_A\mathrm{C}_0 - K_1\mathrm{C}_0$ $+ K_1K_3K_A\mathrm{C}_0^2 + 1 + K_1K_2K_A$	$K_3\mathrm{C}_0 + K_4\mathrm{C}_0 - K_1\mathrm{C}_0 + 1$	$1 - K_1\mathrm{C}_0 - K_DK_1\mathrm{C}_0^2 - K_DK_2K_1\mathrm{C}_0 + K_4\mathrm{C}_0$ $+ K_DK_4\mathrm{C}_0^2 + K_DC_0 + K_3\mathrm{C}_0$
q	$K_3\mathrm{C}_0 + K_4\mathrm{C}_0 + 2 + K_1K_2K_3K_A\mathrm{C}_0$ $+ K_1K_2K_4K_A\mathrm{C}_0 + 2K_1K_2K_A$	$K_3\mathrm{C}_0 + K_4\mathrm{C}_0 + 2$	$2 + K_DK_1\mathrm{C}_0^2 + K_4\mathrm{C}_0 + K_D\mathrm{C}_0 + K_3\mathrm{C}_0$
s	$K_1\mathrm{C}_0 + 1 + K_1K_2K_A$ $K_A = k_{-2}/k_1$	$K_1\mathrm{C}_0 + 1$	$1 + K_1\mathrm{C}_0 + K_DK_2K_1\mathrm{C}_0$ $K_D = k_{-2}/k_3$

regardless of which step is rate controlling. The smaller catalyst pellets would be less diffusion limited and if we take $[C_0]$ to be large at the limit when no diffusion resistance exists then we may expect that under those conditions for the mechanism assuming the bond breaking step to be rate controlling:

$$\frac{p'}{s'} \rightarrow \frac{K_3 + K_4 - K_1}{K_1}, \qquad \frac{q'}{s'} \rightarrow \frac{K_3 + K_4}{K_1}. \tag{9}$$

Analogous results are obtained for the other two rate-controlling steps and are tabulated in Table 2.

Method

The apparatus used in this study consisted of a static bed, plug flow reactor. The catalyst was a LaY zeolite made by exchanging Linde SK40 sieves in a $LaCl_3$ solution until no more Na^+ was exchanged. Both equipment and catalyst preparation have been described in greater detail previously (*8*). Three catalyst sizes were used to examine the effects of intraparticle diffusion on cumene cracking: 20/25, 40/45, and 70/80 mesh. Since the effects of diffusion limitations are more significant at higher temperatures, a reaction temperature of 500°C was used. Conversions were studied at 500°C at four cat/oil values of 0.008, 0.015, 0.030, and 0.050 for each size of catalyst. The times-on-stream were varied between 100 and 600 sec.

The 70/80 mesh catalyst, being least diffusion limited, was then used to investigate the effects of temperature on the parameters of the cumene cracking model. Three reaction temperatures 360, 430, and 500°C were used in this study. At each temperature, three cat/oil ratios were used and time-on-stream was again varied between 100 and 600 sec. All runs were randomized with respect to temperature, mesh size and cat/oil in order to eliminate trends in the experimental data.

Results

The cumene cracking model as described in the introduction was fitted to the experimental results of cumulative cumene conversion against catalyst on stream time. Four parameters were thereby determined—G, N, p', and s'. In keeping with previous work we have selected the bond-breaking step as the rate-controlling step and have, therefore, assumed that $q' = p' + s'$. All computations were performed on an IBM 360 computer using a minimum sum of

TABLE 2
Effect of Diffusing on Model Parameters p'/s' and q'/s'

Rate-controlling step	Increasing particle size	Decreasing particle size
1. Bond breaking	$p'/s' \rightarrow 1$	$p'/s' \rightarrow \frac{K_3 + K_4 - K_1}{K_1}$
	$q'/s' \rightarrow 2$	$q'/s' \rightarrow \frac{K_3 + K_4}{K_1}$
2. Adsorption	$p'/s' \rightarrow 1$	$p'/s' \rightarrow \frac{K_3 + K_AK_3K_2K_1 + K_4}{K_1} + \frac{K_1K_2K_4K_A - K_1 + K_1K_3K_A}{K_1}$
	$q'/s' \rightarrow 2$	$q'/s' \rightarrow \frac{K_3 + K_4 - K_1K_2K_3K_A + K_1K_2K_AK_4}{K_1}$
3. Desorption	$p'/s' \rightarrow 1$	$p'/s' \rightarrow \frac{K_3 + K_D + 2K_DK_4 + -K_DK_2K_1 - K_DK_1 - K_1}{K_1 + KK_2K_1}$
	$q'/s' \rightarrow 2$	$q'/s' \rightarrow \frac{K_DK_1 + K_4 + K_D}{K_1 + K_DK_2K_1}$

TABLE 3

Parameter Estimates for the Cumene Cracking Model for Various Reaction Temperatures and Catalyst Sizes

Temperature (°C)	Mesh size	G (sec^{-1})	Parameters[a] N	p'	s'	SSR
360	70/80	.224	.906	.00204	.000946	.00207
430	70/80	.103	.996	.00226	.000353	.0137
500	70/80	.0313	1.12	.00203	.000134	.0115
500	40/45	.0253	1.00	.00337	.00471	.00389
500	20/25	.0145	1.00	.0045	.00234	.0179
if parameter N is set to 1.0, the results are:						
360	70/80	.1644	(1.0)	.00204	.000946	.00242
430	70/80	.1088	(1.0)	.00180	.000437	.0154
500	70/80	.0424	(1.0)	.00203	.000137	.0121
500	40/45	.0263	(1.0)	.00335	.000469	.00411
500	20/25	.0145	(1.0)	.0045	.00234	.0179

[a] $G = (m - 1)k_d[S_0]^{m-1}[P]$, $p' = px_e^2/k_2[S_0]K_1[C_0]$, $s' = sx_e^2/k_2[S_0]K_1[C_0]$.

squares of residuals as the criterion of fit. A residual was defined as the difference between the cumulative conversion predicted by the model and that determined experimentally. The "least squares" parameter values were determined using Powell's algorithm (*10*).

The optimum values of G, N, p', and s' at each temperature and mesh size are presented in Table 3. The theoretical curves obtained using these values are shown in Figs. 2–6 along with the experimental data.

Clearly if we had chosen one of the other steps to be rate controlling we would have had to fit a five-parameter model (including q') to the data. Since the data were well represented by the four-parameter model, it is doubtful if meaningful results would have been obtained by introducing an additional parameter into the fitting procedure. In point of fact, the model is well fitted using three parameters and setting $N = 1$. The four-parameter fitting is, therefore, shown only to show the effect of adding the extra parameter and to

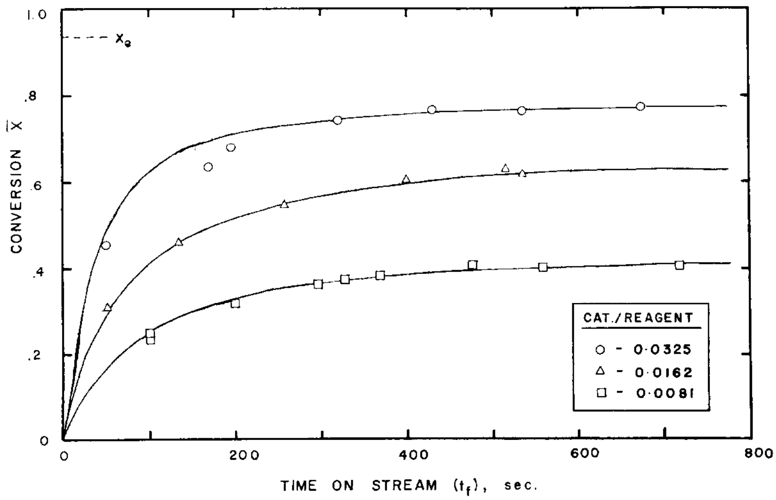

Fig. 2. Least-squares fit of cumene conversion data on 20/25 mesh LaY at 500°C.

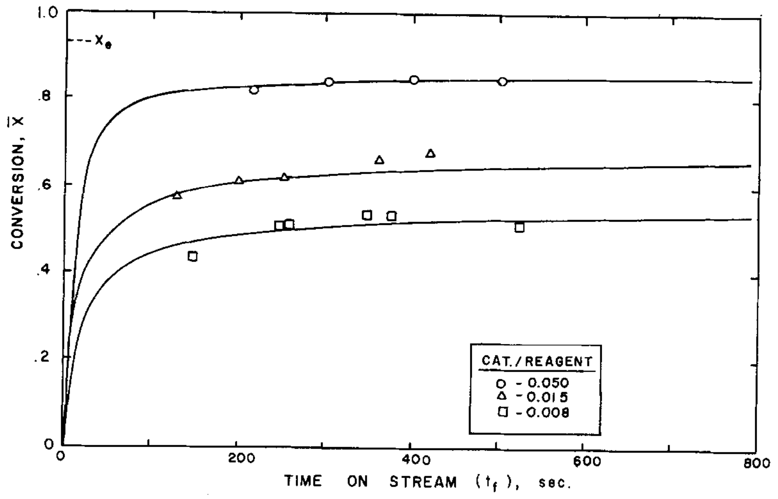

FIG. 3. Least-squares fit of cumene conversion data on 40/45 mesh LaY at 500°C.

discover how far the value of N will deviate from one when it is allowed to assume its optimum value.

DISCUSSION

The ability of the cumene cracking model to fit experimental data has been tested previously (*11*, *12*). This work provides additional evidence of the validity of the model. The model fits the data within the 95% confidence interval for each temperature and mesh size.

The species Y and Z in the mechanism can be identified by examining the reverse reaction. Workers who have studied the alkylation mechanism (*13*, *14*, *4*) maintain that the reaction proceeds by a Rideal mechanism between an adsorbed propylene molecule and a molecule of benzene in the gas phase. Thus Y must be propylene while Z is benzene. That benzene is more strongly adsorbed on an active site appears to be irrelevant (*4*).

That identical rate expressions result for the three potential rate controlling steps is not a surprise. Hutchinson *et al.* (*16*) report that for a monomolecular catalytic reaction having only products and reactants present, and assuming Langmuir–Hinshelwood kinetics, the same mathematical expression to describe the overall rate of reaction results regardless of which

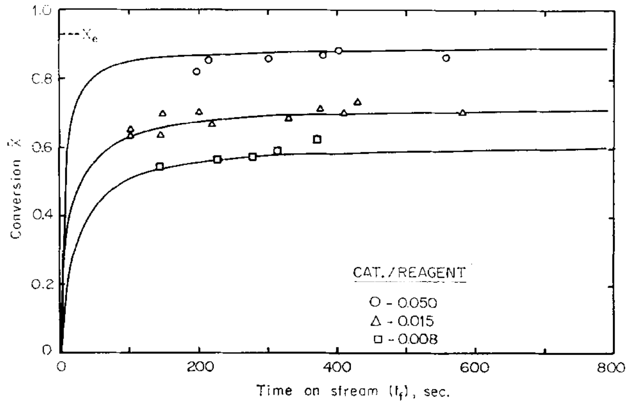

FIG. 4. Least-squares fit of cumene conversion data on 70/80 mesh LaY at 500°C.

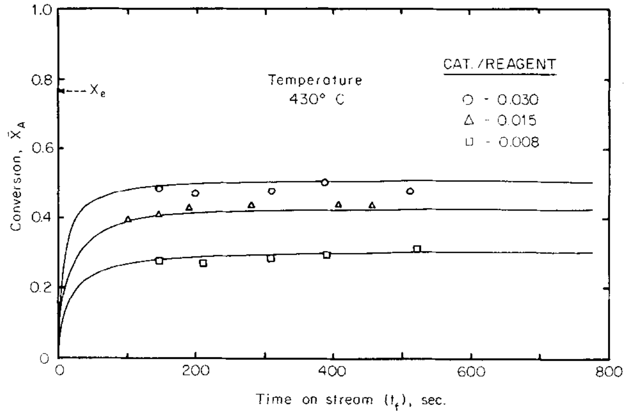

FIG. 5. Least-squares fit of cumene conversion data on 70/80 mesh LaY at 430°C.

step or combinations of steps is rate controlling. Our results concur with Hutchinson's despite the fact we have used a more complex kinetic expression and have accounted for aging. Because our model is valid for any rate-controlling step in the reaction, we need test only one equation in fitting the data. However, this advantage is offset by the disadvantage that it is not possible to determine which step is rate controlling by a kinetic analysis of the rate of reaction.

If we assume the bond breaking step is rate controlling (*1*, *13*, *17–20*), then the parameters of the model are of the form shown in Eqs. (7) and (2). The theoretical ratios p'/s' and q'/s' are given by Eq. (9). The experimentally determined values of p'/s' and q'/s' are shown in Fig. 7. As explained in the introduction $p'/s' \rightarrow 1$ and $q'/s' \rightarrow 2$ with increasing particle size. Decreasing the particle size results in an increase of both ratios to the value of 15.9 and 16.9 for p'/s' and q'/s', respectively.

To illustrate the procedure we propose for interpreting the above observations, we first note that the 70/80 mesh catalyst though still limited by diffusion is expected to be the least diffusion limited of the ones used in this study. Assuming for now that this catalyst is sufficiently close to being diffusion free we can write

$$\left(\frac{p'}{s'}\right)_{70/80\text{ mesh}} \approx (K_3 + K_4 - K_1)/K_1,$$
$$\left(\frac{q'}{s'}\right)_{70/80\text{ mseh}} \approx (K_3 + K_4)/K_1. \tag{10}$$

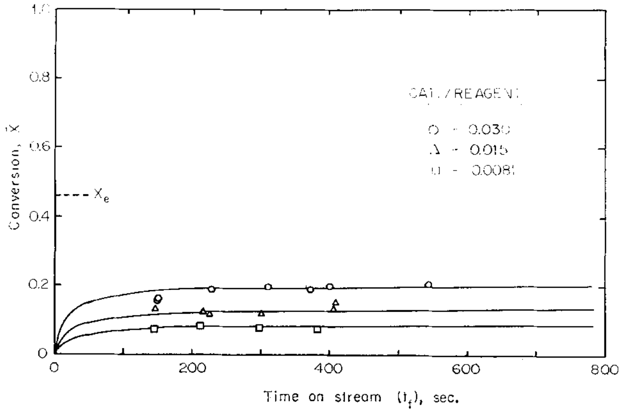

FIG. 6. Least-squares fit of cumene conversion data on 70/80 mesh LaY at 360°C.

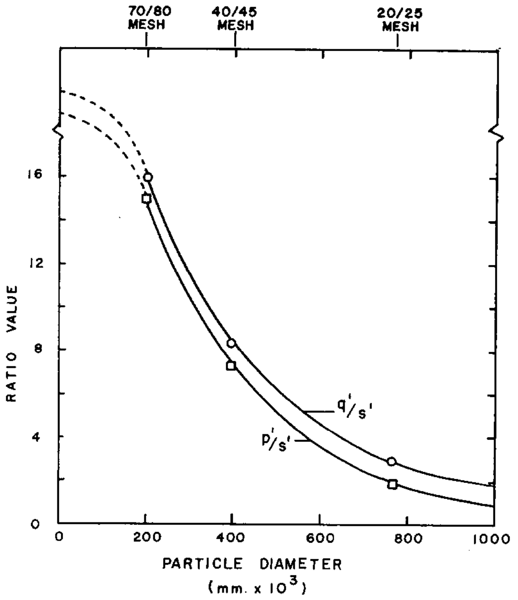

FIG. 7. The effects of particle diameter on the ratios p'/s' and q'/s' at 500°C.

Now, in adsorption studies (*21, 22*), it has been found that benzene is much more strongly adsorbed than propylene. In this case, $K_4 \gg K_3$ and (10) becomes

$$\begin{aligned} p'/s' &\sim (K_4/K_1) - 1, \\ q'/s' &\sim K_4/K_1. \end{aligned} \tag{11}$$

Relation (11) can be written in an alternate form by recalling the thermodynamic representation for equilibrium constants:

$$\begin{aligned} K &= \exp(\Delta G/RT) \\ &= \exp(-\Delta S/R)\exp(\Delta H/RT), \end{aligned}$$

where ΔG = Gibbs free energy, ΔS = entropy of adsorption, and ΔH = enthalpy of adsorption. Using this definition of K, q'/s' becomes

$$\left(\frac{q'}{s'}\right)_{70/80} = \exp\left(\frac{\Delta S_c - \Delta S_z}{R}\right) \exp\left(\frac{\Delta H_z - \Delta H_c}{RT}\right) \tag{12}$$

This equation has been fitted to experimental values of $q'/s'_{70/80}$ for the various reaction temperatures with the result

$$(q'/s')_{70/80} = 1.82 \times 10^4 e^{-11.4\times 10^3/RT}. \tag{13}$$

A comparison of Eqs. (12) and (13) suggests that the heat of adsorption of cumene ΔH_c, exceeds the heat of adsorption of benzene ΔH_z, by 11.1 kcal/mole. Adsorption studies by Boreskova (*21*) confirm that this is reasonable. She found the difference with synthetic zeolites to be approximately 9 kcal/mole. Comparing the pre-exponential terms, it is seen that

$$\Delta S_c - \Delta S_z = 19.5 \text{ cal/mole deg.} \tag{14}$$

In a more fundamental form

$$\begin{aligned} \Delta S_z &= S_{sz} - S_s - S_z, \\ \Delta S_c &= S_{sc} - S_s - S_c, \end{aligned}$$

where S_{sz} and S_{sc} represent the entropy of the adsorbed benzene and cumene molecules, S_s the active-site entropy and S_z and S_c the gas phase entropy of benzene and cumene. Substituting Eq. (15) into Eq. (14) with the appropriate values for S_z and S_c yields

$$S_{sc} - S_{sz} = 65.1 \text{ cal/deg mole at } 300°\text{C}.$$

The corresponding values of $S_{sc} - S_{sz}$ for the other reaction temperatures are tabulated in Table 4, along with the values of $S_c - S_z$. Since the chemisorbed complex is not well understood and because there is insufficient data available on the entropy of adsorption, conclusions drawn from this result have to be tentative at this stage. However the fact that $S_{sc} - S_{sz} > S_c - S_z$ implies a more disordered arrangement of the adsorbed cumene molecule, relative to adsorbed benzene. This entropy difference is greater in the adsorbed state than it is in the gas phase, possibly because of the many more adsorbed configurations possible

TABLE 4

ENTROPY OF ADSORPTION DIFFERENCE FOR CUMENE AND BENZENE CALCULATED FROM EXPERIMENTAL DATA AND EQ. (12)

Temperature (°C)	$S_{sc} - S_{sz}$ (cal deg^{-1} mole^{-1})	$S_c - S_z$ (cal deg^{-1} mole^{-1})
360	65.1	44.1
430	68.3	48.7
500	71.5	53.1

for cumene compared to those possible for benzene (Fig. 8).

The ratio curves as they appear in Fig. 7 can be used to detect significant intraparticle diffusion limitations for the cumene cracking reaction, but cannot isolate the diffusion free regime. With decreasing diffusion resistance, [C_0] throughout the particle will approach a constant value corresponding to the concentration of reactants in the bulk phase. Equation (9) will then become valid with the consequent levelling of the ratio curves shown by the dashed lines in Fig. 7. The sloping portion of the curve to the right of the dashed line is the region where average [C_0] is a function of particle size and hence represents diffusion-limited conditions. The 70/80 mesh catalyst according to this analysis is, therefore, still diffusion limited at 500°C. The conventional test used to isolate the diffusion-free regime is to plot conversion against catalyst particle size at constant conditions, (Fig. 9). The diffusion-free region corresponds to the catalyst sizes for which conversion is constant. This test has a disadvantage in that its sensitivity is dependent on the cat/oil ratio. Maximum sensitivity with this test is obtained at cat/oil ratios small enough that conversion is far from equilibrium. It can be seen from Fig. 9 that this test also suggests that the reaction on 70/80 LaY is still in the diffusion-controlled regime.

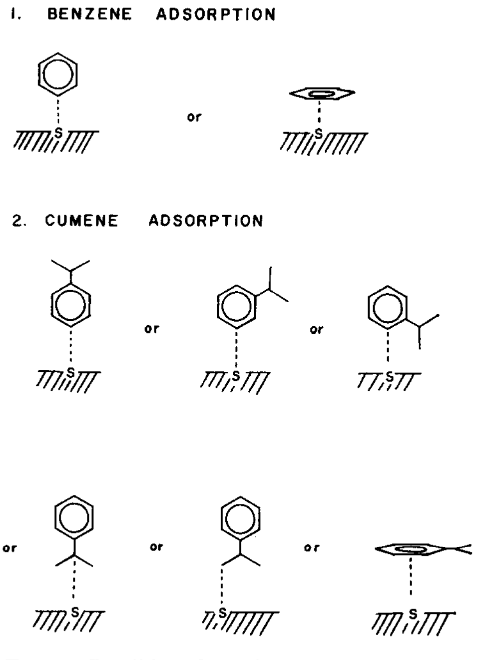

FIG. 8. Possible adsorption modes for benzene and cumene.

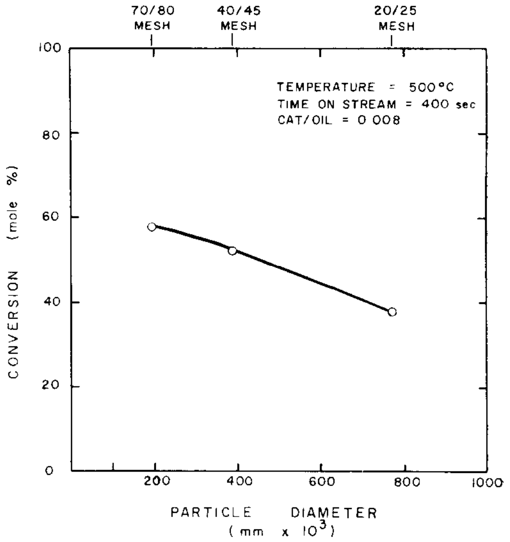

FIG. 9. Effects of mesh size on conversion with all other reaction variables kept constant.

Model Parameters

We now come to examine the model parameters in greater detail. Of the five parameters two, G and N, will be called the aging parameters. The remaining three, p', s', and q' are the kinetic parameters.

(i) The kinetic parameters. The kinetic parameters consist of the intrinsic rate constants, initial concentration of active sites, and adsorption equilibrium constants. Continuing the assumption that the bond-breaking step is rate limiting, these parameters are written as in Eq. (2). In its full form, s' can be written

$$s'/x_e^2 = (K_1[C_0] + 1)/k_2[S_0]K_1[C_0]. \quad (16)$$

In this work, [C_0] $\sim$ 1 atm for a catalyst with minimal diffusion resistance while from adsorption studies (*21*, *22*), it has been found that $K_1 \gg 1$. With these approximations s'/x_e^2 reduces to

$$s'/x_e^2 = [C_0]/k_2[S_0] \text{ sec} \qquad (17)$$

which should yield a straight line on an Arrhenius plot. Experimental values of $\ln(s'/x_e^2)$ for the 70/80 mesh catalyst have been plotted against inverse temperature in Fig. 10. As seen by this plot, the data can in fact be represented by a straight line for which the temperature relationship is:

$$s'/x_e^2 = 3.40 \times 10^{-11} e^{23.5 \times 10^3/RT} \text{ sec}, \qquad (18)$$

i.e., $k_2[S_0]/[C_0]$

$$= 3.24 \times 10^{10} \exp(-23.5 \times 10^3/RT) \text{ sec}^{-1}$$

$$k_2[S_0] = 1.83 \times 10^5 \exp(-22.1 \times 10^3/RT) \text{ mole/g sec.}$$

In Table 5 the activation energy for the bond-breaking step determined in this work is compared with corresponding values reported in literature. From this, it is clear our activation energy for k_2 is consistent with those reported by others. As expected, it exceeds the value reported by Campbell (*8*) because it is felt he operated in a region of significantly greater pore diffusion. Since we have shown that the 70/80 mesh catalyst used in this work is diffusion limited, as indicated by Figs. 8 and 9, the value of 22.1 kcal/mole for the activation energy is a lower limit to the true value. That the value of E_2 for this work is consistent with others listed in Table 5 implies that these workers might also have been using a diffusion-limited catalyst.

TABLE 5

ACTIVATION ENERGIES FOR THE BOND BREAKING STEP FOR CUMENE CRACKING

E_2	Catalyst	Reference
20.6	Cogelled silica alumina	(*19*)
23.6	Cogelled silica alumina (12.4% alumina)	(*18*)
23.4	Cogelled silica alumina (10% alumina)	(*17*)
19.5	Silica alumina molecular sieve (La^{3+})	(*11*)
28.2	Cu^{2+} silica alumina molecular sieve	(*26*)
22.1	La^{3+} silica alumina molecular sieve	This work
24.0	H^+ form of Linde Y type zeolite	(*27*)

From Fig. 11 it is seen that the largest pre-exponential term (i.e., the k_2 $[S_0]$ intercept) is that obtained for this work. This suggests that more active sites are available on the La^{3+} zeolite than on the cogelled silica alumina catalyst used by Horton (*17*) Maatman (*18*) or Pansing (*19*). This interpretation is confirmed by the results of Horton (*17*). A pre-exponential term for this work larger than that obtained by Campbell is consistent with our intuitive understanding of the diffusion process. Large, diffusion-limited catalyst particles would have internal active sites that would see $[C_0] \rightarrow 0$ and, therefore, remain vir-

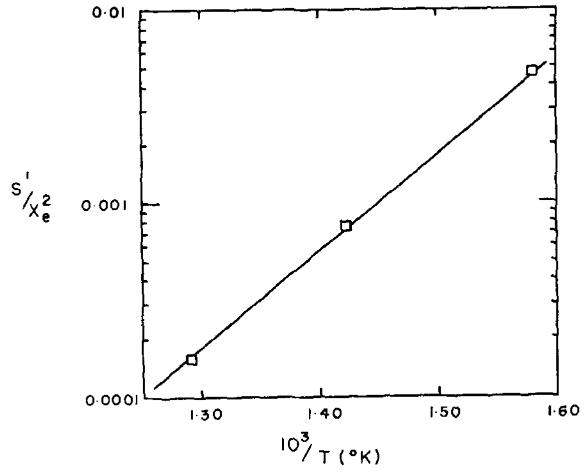

FIG. 10. An Arrhenius plot of parameter s'/x_e^2.

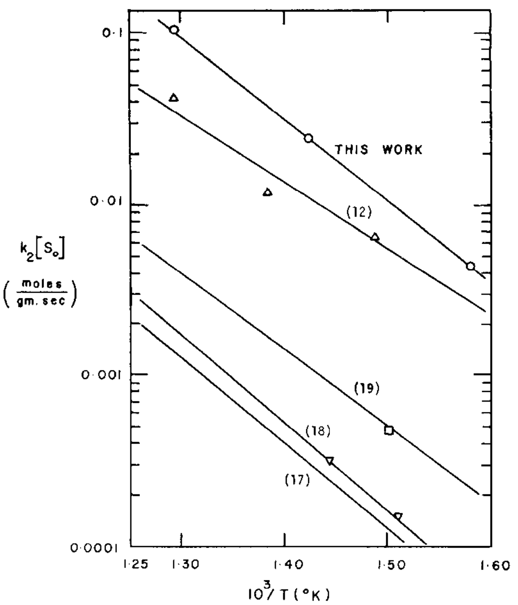

FIG. 11. A comparison of $k_2[S_0]$ for this work to some reported in literature. Numbers in parenthesis indicate references.

tually unused. The diffusion-free catalyst on the other hand has these active sites available and hence the reaction uses a greater concentration of sites per unit catalyst weight.

(ii) The aging parameters. The parameter N has been defined (*5*) as

$$N = n/(m - 1), \qquad (19)$$

where m = number of sites lost per deactivation event and n = number of sites used per cracking event.

The least-squares value for N for the various reaction conditions is shown on Table 3. For the 500°C data, N was found to be approximately 1.0. For the 70/80 mesh catalyst, N decreased with decreasing temperature. This occurs because the time required to reach a level of constant conversion is greater at lower temperatures and hence our data do not give a very good value of N. Conversions from auxiliary runs at long on-stream times confirmed that a constant conversion was indeed obtained. Thus a value of 1.0 for N at all temperatures and mesh sizes is correct and the system shows Class II behavior (*23*).

The significance of N equal to one, or Class II aging behavior is as follows. It is generally believed that cumene cracking occurs with the chemisorption of a cumene molecule on a single active site (*8*, *17–20*). In that case, $n = 1.0$. Since $N = 1$ for all temperatures we calculate that $m = 2$. Such a value of m implies either a Hinshelwood deactivation mechanism in which two sites are lost per deactivation event, or that the deactivation proceeds by the adsorption of a poison on two sites. That m is two for all catalyst sizes implies that diffusion has no effect on the mechanism of aging. Intuitively, this result appears correct since diffusion is strictly a transport phenomenon affecting the flow of molecules to the active sites on the catalyst and would not be expected to affect the mechanism of aging.

It has been postulated (*8*) that the decay is a consequence of the dimerization of two adsorbed propylene molecules and their subsequent dehydrogenation. However, adsorption and thermodynamic arguments based on a dimerization mechanism of poisoning indicate that propylene cannot be the poison whereas cumene could be. Firstly, the heat of adsorption of propylene on a zeolite catalyst has been found to be of the order of 1 kcal/mole while that for cumene is of the order of 20 kcal/mole (*21*, *22*). This suggests that propylene adsorption is therefore very weak. Secondly, the previously discussed analysis of the entropy of adsorbed cumene indicates that there are many adsorption configurations that cumene is able to assume. It is now suggested that cumene dealkylation occurs only via one of the possible adsorption complexes. The various complexes shown on Fig. 8 can thus have end results such as

1. cracking
2. desorption
3. dimerization with catalyst deactivation
4. disproportionation

The second aging parameter G can be used to define the poisoning species more clearly. G is also a function of temperature

$$G = 1.154 \times 10^{-4} e^{9.2 \times 10^3/RT}\ \text{sec}^{-1}. \qquad (20)$$

A previous analysis of G (*8*) demonstrated that it is a function of two temperature-dependent terms: $[P]$ the poison concentration and k_d, the deactivation rate constant. In its complete form, G is given by

$$G = (m - 1)[P]k_d[\mathrm{S}_0]^{m-1}. \tag{21}$$

If aging proceeds by a two-site Hinshelwood mechanism, then we can write for $[P]$

$$[P] \propto \theta_i^2 = \frac{K_i[C_i]}{1 + K_1[C] + K_3[Y] + K_4[Z]}, \tag{22}$$

where i is the component that is the poisoning agent. If propylene is taken as the i^{th} component in Eq. (22) we get, after simplification

$$[P] \propto A^* \exp(-28 \times 10^3/RT),$$

where $A^* = (K_3°[Y]/K_4°[Z])^2$.

The negative activation energy means the activation energy for k_d would have to be -37 kcal/mole in order to explain the behavior of G. This is unreasonable if we believe k_d to be a kinetic rate constant. A similar development for benzene as the poisoning species results in another unacceptable value for the activation energy of k_d.

On the other hand, if cumene is taken to be the poisoning species,

$$[P] \propto \theta_i^2 = \left(\frac{K_1[C]}{1 + K_1[C] + K_3[Y] + K_4[Z]}\right)^2,$$

which after simplification becomes

$$[P] \propto A^* \exp(22.1 \times 10^3/RT),$$

where $A^* = (K_1°[C]/K_4°[Z])^2$.

This results in an activation energy for k_d of $+12.9$ kcal/mole. There remains the possibility suggested by Prater and Lago (*1*) that an impurity present in the cumene is the poisoning agent. We have not detected any such impurity in our analysis but leave this possibility open. The thing to remember in this case is that if such an impurity is responsible for catalyst decay then removal of the impurity would result in a nondecaying system. Such a system has not been observed in cumene cracking in the many studies reported in the literature.

The upshot of our analysis is that $[P]$, the concentration of poison, is a function of temperature and that cumene is the most likely poison in the reaction. It should be made clear, however, that $[P]$ represents poisons, not coke. $[P]$ is only the precursor of coke.

If θ is defined as the instantaneous fraction of active sites remaining at time t, then from Eq. (5),

$$\theta = [S]/[S_0] = (1 + Gt)^{-N}.$$

The fraction of active sites lost by the end of the run is given by

$$(1 - \theta_f) = 1 - (1 + Gt_f)^{-N}. \tag{23}$$

An analysis of $(1 - \theta_f)$ (Fig. 12), indicates that the catalytic activity is not directly related to coke on catalyst. This does not imply that coke has no influence on the activity loss of the catalyst. It is only to say that the loss of activity is not merely a question of how much coke is deposited, but how it is deposited. "Coke" as obtained by conventional analysis may include adsorbed species which do not in any way contribute to deactivation.

Energetics of Cumene Cracking

We can now summarize the consequences drawn up to this point by considering the energetics of cumene cracking. This analysis leads to some unexpected conclusions.

Figure 13 shows a sketch of the energy profile for the cracking of cumene. Values taken from literature sources are identified by reference numbers. It is clear from this figure that if the values used here are taken to be correct, we are driven to the conclusion that the activation energy for cumene cracking will be on the order of 54 kcal/mole. Further considerations of this value leads to the conclusion that if this activation energy applies, the catalytic reaction would be slower than the thermal decomposition of cumene.

We therefore arrive at the conclusion that some of the values taken from the literature are incorrect. Since the ΔE value represents a well-established thermodynamic quantity, suspicion is cast on the

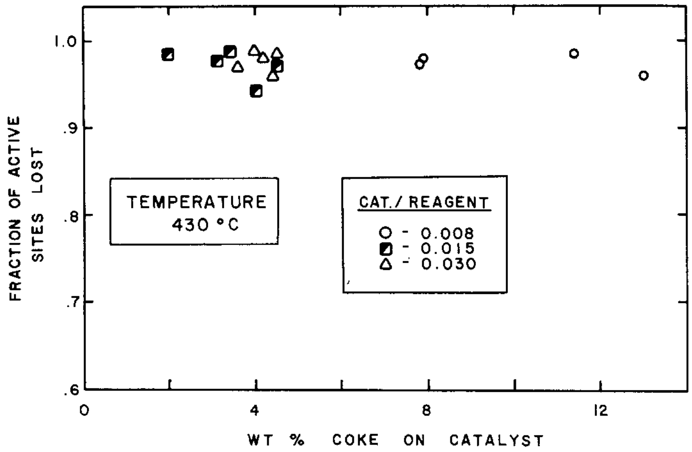

FIG. 12. Fraction of active sites lost at the end of a run, $(1 - \theta_f)$ plotted against weight percent coke on catalyst.

heats of adsorption and the activation energy for alkylation.

The activation energy for alkylation is likely to be wrong if the studies of Panchenkow *et al.* (*24*) were also done on a diffusion-limited catalyst. This, however, will not help us since the true activation energy for alkylation in that case will be higher than 14 kcal/mole.

On the other hand, we can readily expect that the heats of adsorption reported in the literature and used here are not applicable. After all, none of the heats reported concerns the heat of formation of carbonium ions, but rather the heat of physical adsorption. It can be expected that the formation of a carbonium ion is in fact an endothermic process leading to energy levels

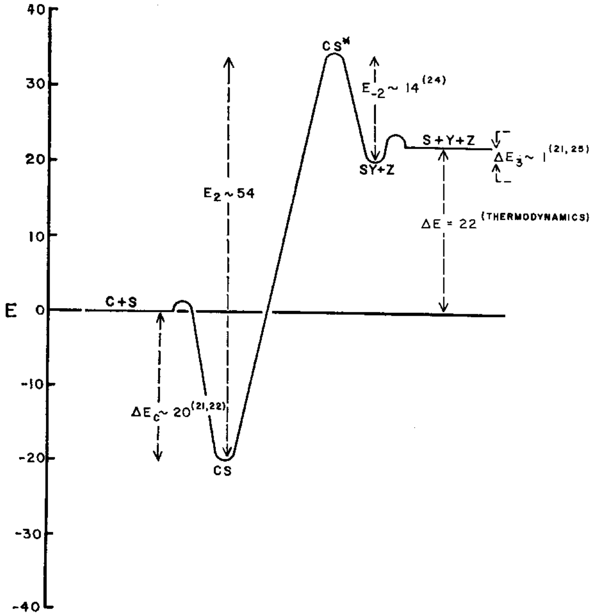

FIG. 13. Energy diagram for the catalytic cracking of cumene based on energy values reported in literature. Numbers in parentheses indicate references.

for CS and SY + Z lying above those for C + S and S + Y + Z, respectively. In fact if $\Delta E_c = \Delta E_y$ the minimum activation energy for cumene cracking would be 22 + 14 = 36 kcal/mole. This value would be less if $\Delta E_c > \Delta E_y$ which we might expect or greater if $E_{-2} > 14$ kcal/mole as suggested above. However, even a value of $E_2 = 36$ kcal/mole will make the catalytic rate of reaction considerably greater than that for thermal cracking.

By this analysis we are once more left without a value for the real activation energy for the cracking of cumene. However, we feel an important step forward has been taken with the realization that diffusion control is frequently present in this reaction and, furthermore, that such reactions require a value of the heat of formation of the carbonium ion to be determined before their energetics can be successfully studied.

CONCLUSIONS

It is shown that the Campbell–Wojciechowski model adequately represents cumene conversion data over a wide range of temperatures, cat/oil ratios, and diffusion limitations. Using the parameters of the model, a new test is introduced to allow study of the extent of mass transfer resistance within a catalyst particle in cumene cracking. It is thus shown that results reported by previous authors for this reaction may have been obtained on diffusion-limited catalysts.

From our analysis, it has been determined that the heat of adsorption of cumene exceeds the heat of adsorption of benzene by 11 kcal/mole at 500°C. This implies that cumene is adsorbed more strongly than benzene. The entropy difference between cumene and benzene in the adsorbed phase is shown to be positive and larger than the corresponding difference of the gas-phase species. This can be explained by noting that cumene has more modes of adsorption than benzene.

It is shown that diffusion has no effect on the mechanism of catalyst aging. This conclusion is based on the observation that the parameter N remains constant despite changing mass-transfer resistance.

The lower limit of the activation energy for the bond breaking step has been found to be 22.1 kcal/mole. As this value agrees favorably with the findings of other workers, we suspect that these workers were also using diffusion limited catalysts. Unfortunately, it will be difficult to determine the diffusion free value for pure catalyst in a plug flow reactor as the catalyst is diffusion limited down to particle sizes which make a packed bed so dense that pressure-drop complications become serious.

In this paper we present thermodynamic arguments which indicate that if site poisoning proceeds by the dimerization of two adsorbed species then only the dimerization of adsorbed cumene can explain the observed results. Work on the specific mechanism of site poisoning is presently in progress and we should soon be in a position to define the chemistry of the poisoning reaction.

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