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Catalytic Cracking of Cumene on Aging Catalysts

I. The Mechanism of the Reaction

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A general mechanism for the catalytic cracking of cumene is proposed. The mechanism is used to develop a rate expression for the reaction on an aging catalyst, using the time-on-stream theory of catalyst decay. This approach takes into account the initial rapid loss of catalyst activity during the reaction. The model predicts three classes of catalyst aging behavior which are consistent with those predicted previously using a much simpler mechanism.

NOMENCLATURE

C	cumene
[C]	concentration of cumene
K	equilibrium constant
G, N	aging parameters
P	catalyst/reagent ratio
S	active site
Y,Z	products (benzene and propylene)
k	reaction rate constant
$-r_c$	rate of disappearance of cumene
t	catalyst time-on-stream
x	fractional conversion
$\bar{x}$	integral or cumulative conversion
ϵ	expansion coefficient
θ	fraction of active sites occupied
τ	space time

Subscripts

1, 2, etc.	refer to component reactions
c, y, z	species involved in the reaction
e	equilibrium conditions
f	final conditions
0	initial conditions

INTRODUCTION

The catalytic cracking of cumene to benzene and propylene takes place with the formation of a minimum of by products. Kinetic investigations of this reaction are thus facilitated by the stoichiometric simplicity of the reaction as well as by the slow aging of the cracking catalyst.

In an early paper by Corrigan *et al.* (*2*), it was suggested that catalytic cracking of cumene proceeds by a surface reaction in which the cumene is chemisorbed on a single active site, splits off propylene into the gas phase, and finally benzene is desorbed from the surface. Corrigan dismissed the reverse reaction, the alkylation of benzene by propylene, as negligible under his experimental conditions.

Later, Plank and Nace (*3*) considered the effects on cumene cracking of reversible and irreversible poisoning of the catalyst. They observed a rapid initial decline in the cracking rate which they explained as the period during which equilibrium adsorption of "inhibitor" on the catalyst is established. After about 10 min of operation the rate of the cracking reaction becomes approximately constant. Most mechanistic studies, including that of Plank and Nace, have been attempted in the region of "constant" rate of reaction. Prater and Lago (*4*) as well as Horton and Maatman (*5*) reported a similar rapid decay of catalyst activity during the initial 10 min of operation, despite the fact that the latter investigators used differential reactors while Plank and Nace worked with an integral reactor.

The basic mechanism of the reaction can be written

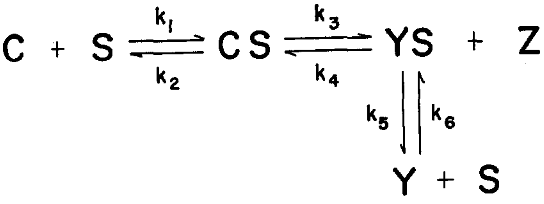
$$C + S \rightleftharpoons CS \rightarrow \text{products},$$

where C is cumene, S is an active site and CS is chemisorbed cumene on an active site. Such a mechanism has been accepted by Plank and Nace, Prater and Lago, and Horton and Maatman in a region of conversion where the reverse reaction is negligible. Prater and Lago also proposed an extended mechanism of the reaction written to include the effect of the reverse reaction but did not test it against experimental data.

In our studies we have used the cracking of cumene as a method of studying the aging of a cracking catalyst. In practice commercial cracking catalysts are on stream for periods of less than 10 min and hence the region of interest is the one which has been avoided by previous authors, the period of rapid catalyst decay. In this paper we develop a model of the reaction which is consistent with previous models, describes the cracking of cumene at high conversions (i.e., near equilibrium), and accounts for catalyst aging effects.

THEORY

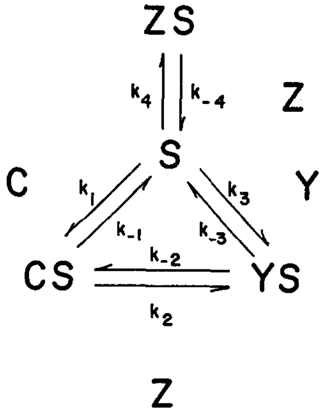
The catalytic cracking of cumene commences with the chemisorption of cumene on a single active site. This is followed by the splitting of the molecule to propylene and benzene. The reverse reaction, the alkylation of benzene to cumene requires the adsorption of either benzene or propylene on an active site followed by combination with the appropriate gas phase component by a Rideal mechanism. Based on this, Prater and Lago (*4*) proposed the following mechanism of the reaction



where C is cumene, S is an active site, Y and Z are products.

It was assumed that the rate of desorption of both cumene and component Y is fast compared with the bond breaking or bond formation step. Thus equilibria exist between the gas phase species and their surface complexes. It should be noted that Prater and Lago's mechanism also assumes that one product, Z, is not adsorbed on the catalyst surface.

Prater and Lago's mechanism is here expanded to account for the adsorption of all three components on the catalytic sites. This mechanism can be written



The △ mechanism is consistent with Prater and Lago's assumptions, and we feel that it represents a more general case. In our mechanism adsorption equilibria between all gas phase species (C, Y, and Z) and the active sites, S, are assumed to exist. The adsorption equilibrium constants are defined such that

$$K_c = \frac{k_1}{k_{-1}} = \left[\frac{[CS]}{[C][S]}\right]_{eq}, \tag{1a}$$

$$K_y = \frac{k_3}{k_{-3}} = \left[\frac{[YS]}{[Y][S]}\right]_{eq}, \tag{1b}$$

$$K_z = \frac{k_4}{k_{-4}} = \left[\frac{[ZS]}{[Z][S]}\right]_{eq}. \tag{1c}$$

The fraction of sites covered by each component is written using the Langmuir adsorption isotherms:

$$\theta_c = \frac{[CS]}{[S_0]} = \frac{K_c[C]}{1 + K_c[C] + K_y[Y] + K_z[Z]}, \tag{2a}$$

$$\theta_y = \frac{[YS]}{[S_0]} = \frac{K_y[Y]}{1 + K_c[C] + K_y[Y] + K_z[Z]}, \tag{2b}$$

$$\theta_z = \frac{[ZS]}{[S_0]} = \frac{K_z[Z]}{1 + K_c[C] + K_y[Y] + K_z[Z]}. \tag{2c}$$

The rate of disappearance of cumene is written

$$-r_c = k_2[CS] - k_{-2}[YS][Z]. \tag{3}$$

Substitution for [CS] and [YS] in Eq. (3) from Eqs. (2a) and (2b), respectively, yields

$$-r_c = \frac{k_2K_c[C][S_0] - k_{-2}K_y[Y][Z][S_0]}{1 + K_c[C] + K_y[Y] + K_z[Z]}. \tag{4}$$

The above rate equation can be expressed in terms of the fractional conversion of cumene, x, by substituting into Eq. (4) the following expressions relating concentration of the components and fractional conversion of cumene *(6)*.

$$[C] = [C_0]\left(\frac{1 - x}{1 + \epsilon x}\right), \tag{5a}$$

$$[Y] = [Z] = [C_0]\left(\frac{x}{1 + \epsilon x}\right), \tag{5b}$$

where x is fractional conversion and ϵ is the expansion coefficient for the reaction. ($\epsilon = 1$ for this reaction).

$$-r_c = \frac{k_2K_c[S_0][C_0]\left(\frac{1 - x}{1 + x}\right) - k_{-2}K_y[S_0][C_0]^2\left(\frac{x}{1 + x}\right)^2}{1 + K_c[C_0]\left(\frac{1 - x}{1 + x}\right) + K_y[C_0]\left(\frac{x}{1 + x}\right) + K_z[C_0]\left(\frac{x}{1 + x}\right)}. \tag{6}$$

At equilibrium conditions the following relationship is valid:

$$\frac{k_2}{k_{-2}} = \frac{[Z_e][YS_e]}{[CS_e]}, \tag{7}$$

also from Eq. (1a),

$$[CS_e] = K_c[C_e][S_e],$$

and from Eq. (1b),

$$[YS_e] = K_y[Y_e][S_e],$$

$$\therefore \frac{k_2}{k_{-2}} = \frac{K_y}{K_c} \cdot \frac{[Y_e][Z_e]}{[C_e]} = \frac{K_y}{K_c} \cdot K_e, \tag{8}$$

where K_e is the thermodynamic equilibrium constant for the reaction

$$C \rightleftarrows Y + Z.$$

The thermodynamic equilibrium constant, K_e, can also be expressed in terms of equilibrium conversion using Eq. (5a) and (5b).

$$K_e = [C_0]\left(\frac{x_e^2}{1 - x_e^2}\right). \tag{9}$$

Substituting Eq. (9) into Eq. (8) yields

$$\frac{k_2}{k_{-2}} = \frac{K_y}{K_c}[C_0]\left(\frac{x_e^2}{1 - x_e^2}\right). \tag{10}$$

The rate Equation (6) can now be rearranged by substituting for $k_{-2}K_{-y}$ from Eq. (10) and multiplying the top and bottom by $(1 + x)^2$. The resulting equation after grouping terms is

$$-r_c = \frac{\frac{k_2K_c}{x_e^2}[S_0][C_0](x_e^2 - x^2)}{(K_y[C_0] + K_z[C_0] - K_c[C_0] + 1)x^2 + (K_y[C_0] + K_z[C_0] + 2)x + (1 + K_c[C_0])}. \tag{11}$$

Now, the design equation for a plug flow static bed reactor can be written *(6)*

$$\tau = [C_0]\int_0^x \frac{dx}{-r_c}. \tag{12}$$

Letting $p = K_y[C_0] + K_z[C_0] - K_c[C_0] + 1$,

$$q = K_y[C_0] + K_z[C_0] + 2,$$

$$s = K_c[C_0] + 1$$

(note that $q - p = s$),

Eq. (12) upon the introduction of Eq. (11) becomes

$$\tau = \frac{x_e^2}{k_2K_c[S_0]}\int_0^x \left(\frac{px^2+qx+s}{x_e^2-x^2}\right)dx. \quad (13)$$

Integration of Eq. (13) yields

$$\tau = \frac{x_e^2}{k_2K_c[S_0]}\left(-px+\frac{q}{2}\ln\left(\frac{x_e^2}{x_e^2-x^2}\right) + \left(\frac{px_e^2+s}{2x_e}\right)\ln\left(\frac{x_e^2+xx_e}{x_e^2-xx_e}\right)\right). \quad (14)$$

Solving Eq. (14) for x gives the instantaneous value of fractional conversion of cumene obtained if the space velocity is $1/\tau$ and the active site concentration remains constant at $[S_0]$.

However, our catalyst is in fact subject to loss of active sites due to side reactions which produce coke. This loss of sites can be described by the time-on-stream theory of catalyst decay (*1*) which provides an aging function such that

$$[S] = [S_0]\left(\frac{1}{1+Gt}\right)^N, \quad (15)$$

where $[S_0]^0$ is the concentration of sites initially available. Equation (14) can be readily modified to include the effect of catalyst aging.

$$\tau[S_0]\left(\frac{1}{1+Gt}\right)^N = \frac{x_e^2}{k_2K_c}\left(-px+\frac{q}{2}\ln\left(\frac{x_e^2}{x_e^2-x^2}\right)+\left(\frac{px_e^2+s}{2x_e}\right)\ln\left(\frac{x_e^2+x_ex}{x_e^2-x_ex}\right)\right). \quad (16)$$

Solving for conversion in the above equation again gives an instantaneous value of conversion obtained at a catalyst time-on-stream t and at a space velocity $1/\tau$. The average conversion (or integral conversion) over some period of time from $t = 0$ to $t = t_f$ is found by integrating the instantaneous conversion, x, with respect to time-on-stream from 0 to t_f and time averaging the result.

$$\bar{x} = \frac{1}{t_f}\int_0^{t_f} x\,dt, \quad (17)$$

where $\bar{x}$ is integral conversion.

DISCUSSION

The time-on-stream catalyst aging theory proposed by Wojciechowski (*1*) predicts that three different classes of aging behaviors are shown by catalysts. The numerical value of the aging exponent, N, in Eq. (15) dictates the class into which a given catalyst falls.

Class I: $N < 1$. At a constant catalyst/reagent ratio, increasing the duration of an experimental run from $t_f = 0$ results in an increase in the integral conversion up to the limiting case of complete conversion.

Class II: $N = 1$. At a constant catalyst/reagent ratio, increasing the duration of an experimental run from $t_f = 0$ results in an increase in the integral conversion up to a limiting value less than complete conversion. A further increase in the duration of the run causes no change in conversion from the limiting value.

Class III: $N > 1$. At a constant catalyst/reagent ratio, increasing the duration of an experimental run from $t_f = 0$ results in an increase in conversion up to a maximum value after which a further increase in the time of a run causes a decrease in conversion. These predictions were made on the basis of a very simple reaction mechanism.

Figure 1 is a plot of integral conversion vs time-on-stream for each class of catalyst ($N < 1$, $N = 1$, and $N > 1$) and for the model developed here with all other parameters of the model held constant. It shows that even a complex mechanism such as that discussed in this paper will obey the above classification rules if complete conversion is understood to be equilibrium conversion. The curves were produced by picking suitable values for all the parameters involved in Eq. (16) ($G = 0.02$, $k_2K_c = 1.0$, $x_e = 0.84$, $p = 4.0$, $q = 5.0$, and $s = 1.0$). The final time-on-stream t_f, of a hypothetical experiment is set and related to the space time by the proportionality

$$\tau \alpha P t_f, \quad (18)$$

where P is the catalyst/reagent ratio. The instantaneous fractional conversions at in-

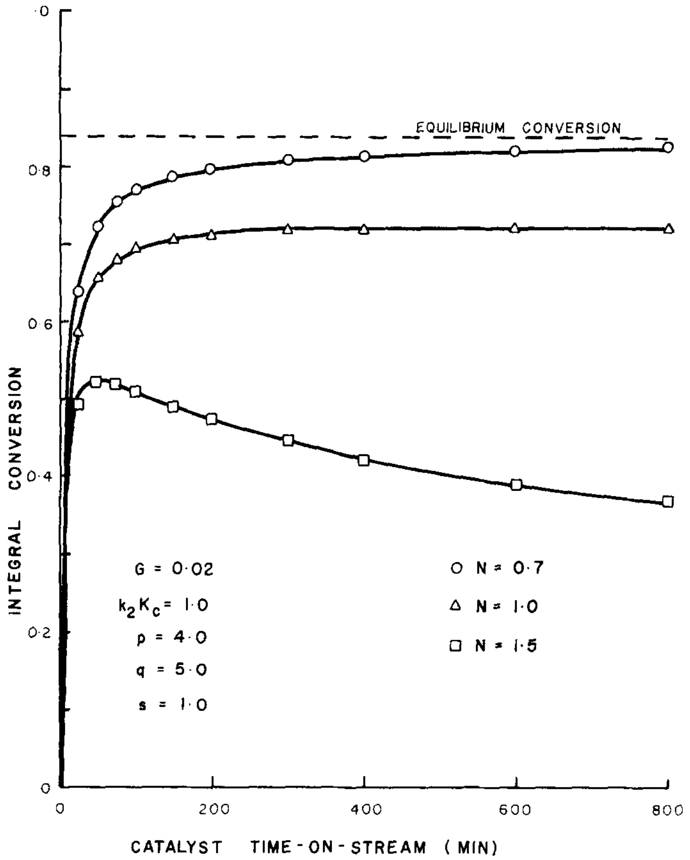


FIG. 1. Functional behavior of Eq. (17) for Class I, II, and III behavior in cumene cracking.

crements of time-on-stream up to t_f are calculated by computer from Eq. (16) by a trial and error method, then integrated and time averaged to obtain the integral conversion as shown in Eq. (17). These calculations give one point on a theoretical integral conversion vs time-on-stream plot and must be repeated using the same catalyst/reagent ratio but a different t_f to obtain other points on the curve.

The validity of our theoretical model of cumene cracking has been tested by experimentation and the results will be reported soon. Figure 1 indicates the specific manner in which experimental data must be prepared. Runs at a constant catalyst–reagent ratio are performed at various final times-on-stream until an experimental integral conversion vs time-on-stream curve is formed. At the same temperature at least two other experimental curves at different catalyst–reagent ratios are desirable as fitting only one curve would not give a good estimate of the parameters of the model. Repeat runs at each experimental point yield estimates of standard deviations of integral conversion from which the goodness of fit of the parameters can be assessed. The repetition of the above experimental design at three or more temperatures provides data for the correlation of parameters which would be expected to follow Arrhenius type relationships. These are the aging rate constant parameter G, the product of constants k_2K_c and K_c itself which can be obtained from s.

CONCLUSIONS

A complete mechanism for the catalytic cracking of cumene has been proposed. This mechanism includes the adsorption–desorption step of all three major reactants (cumene, benzene, and propylene) on the catalyst surface as well as the reversible reaction of chemisorbed cumene to one gas phase and one chemisorbed product. The only assumption which has been made in the development of this mechanism is that the bond breaking and bond formation steps always occur in the same way (i.e., the chemisorbed product of the cracking reaction is always the same).

The reaction of cumene to benzene and propylene generally occurs in the presence of an aging catalyst. The resultant loss of activity of the catalyst during the reaction is here taken into account by the time-on-stream theory of catalyst decay (*1*). From this an equation has been developed which relates instantaneous conversion to the catalyst age. It is also shown how the integral (or cumulative) conversion can be obtained from instantaneous conversion.

Three classes of catalyst aging behaviors were previously established on the basis of a simple first order reaction mechanism (*1*). It is demonstrated that even for the complex case presented here the phenomenological behavior of the integral conversion vs time-on-stream is in agreement with that previously predicted. This suggests that the class of catalyst aging can be readily discerned from integral conversion vs time-on-stream data for any reaction mechanism.

REFERENCES

1. WOJCIECHOWSKI, B. W., *Can. J. Chem. Eng.* **46,** 48 (1968).
2. CORRIGAN, T. E., GARVER, J. C., RASE, H. F., AND KIRK, R. S., *Chem. Eng. Progr.* **49,** 603 (1953).
3. PLANK, C. J., AND NACE, D. M., *Ind. Eng. Chem.* **47** (11), 2375 (1955).
4. PRATER, C. D., AND LAGO, R. M., *Advan. Catal. Relat. Subj.* **8,** 293 (1956).
5. HORTON, W. B., AND MAATMAN, R. W., *J. Catal.* **3,** 113 (1964).
6. LEVENSPIEL, O., "Chemical Reaction Engineering." Wiley, New York, 1962.