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The Catalytic Cracking of Cumene on Aging Catalysts

II. An Experimental Study

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The time on stream theory of catalyst decay is applied to data obtained by cracking cumene on a lanthanum-exchanged Y-sieve catalyst. It is shown that the theory describes the observed phenomena correctly. As a result it can be reported that the system cumene–LaY exhibits Class II behavior and that poisoning reactions remove two active sites per deactivating event. The activation energy for the cracking reaction is found to be 19.5 kcal/gmole.

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}
[I]	concentration of poison, atm
K	adsorption equilibrium constant, atm^{-1}
K_e	chemical equilibrium constant
M	$1/(m-1)$, dimensionless
N	aging exponent, dimensionless
P	catalyst/reagent ratio (weight ratio)
P_b	partial pressure of benzene, atm
P_c	partial pressure of cumene, atm
P_p	partial pressure of propylene, atm
[S]	concentration of active sites at t, $\mathrm{sites/m^2}$
$[\mathrm{S_0}]$	initial concentration of active sites, $\mathrm{sites/m^2}$
T	temperature, °K
Y, Z	products
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
$-r_c$	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

In a previous publication (*1*) we have postulated that cumene is cracked by zeolite catalysts according to the Δ mechanisms shown in Fig. 1. The model assumes that adsorption equilibria exist between C, Y, and Z and the active sites S. Thus, the rate equation for the disappearance of cumene is written

$$-r_c = k_2[\mathrm{CS}] - k_{-2}[\mathrm{YS}][\mathrm{Z}]. \quad (1)$$

After substituting for [CS] and [YS] in terms of Langmuir isotherms, accounting for volume expansion of the reactants, for

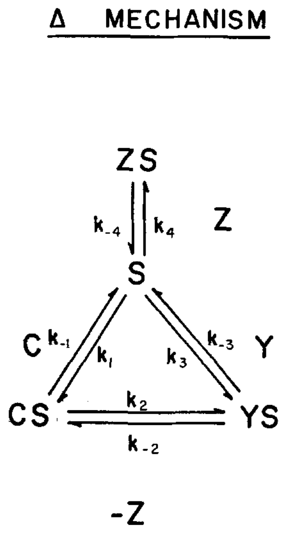

FIG. 1. Δ Mechanism.

thermodynamic equilibrium and for aging, the resultant rate equation was inserted into the design equation for a plug flow static bed reactor. The theoretical development leads us to the equation

$$\tau[\mathrm{S}_0]\left(\frac{1}{1+Gt}\right)^N = \frac{x_e^2}{k_2K_c}\left[-px + \frac{q}{2}\ln\frac{x_e^2}{x_e^2-x^2} + \left(\frac{px_e^2+s}{2x_e}\right)\ln\frac{x_e+x}{x_e-x}\right] \quad (2)$$

where x is the instantaneous conversion of cumene on a catalyst of age t under conditions where the space time* is τ and the equilibrium fractional conversion is x_e. It was also shown that the cumulative conversion $\bar{x}$ in a given run is calculated from

$$\bar{x} = \frac{1}{t_f}\int_0^{t_f} x\,dt, \quad (3)$$

where t_f is the length of the run. The relationship between τ and t_f was formulated previously (*2*):

$$\tau = bPt_f, \quad (4)$$

where b is a constant, τ is the space time based on catalyst bulk volume, P is the catalyst-to-reagent weight ratio, and t_f is the total duration of the run. Equation (4) indicates that, at a constant catalyst-to-reagent ratio, an experiment of longer time-on-stream or duration will result in the reactant being in the presence of the catalyst for a proportionally longer time.

Using Eq. (4) in Eq. (2) and rearranging we arrive at

$$bPt_f\left(\frac{1}{1+Gt}\right)^N = \left[-p'x + \frac{p'+s'}{2}\ln\frac{p'x_c^2+s'}{2x_e}\ln\frac{x_e+x}{x_e-x}\right], \quad (5)$$

where

$$p' = \frac{px_e^2}{k_2[\mathrm{S}_0]K_c},\ p = K_y[\mathrm{C}_0] + K_z[\mathrm{C}_0] - K_c[\mathrm{C}_0] + 1, \quad (6)$$

$$s' = \frac{sx_e^2}{k_2[\mathrm{S}_0]K_c},\ s = K_c[\mathrm{C}_0] + 1. \quad (7)$$

Correlating experimental data with the theoretical model given in Eq. (3) requires the estimation of four parameters: G, the aging constant; N, the aging exponent; p' and s', combinations of the rate constant of the bond-breaking step and the adsorption equilibrium constants for components of the mechanism.

APPARATUS AND EXPERIMENTAL PROCEDURE

The reactor consisted of a Pyrex glass tube approximately 1 in. in diameter and 24 in. long. The tube was wound with asbestos-covered heating wire over several layers of aluminum foil. The top section of the reactor, which functioned as a vaporizer and preheater, was packed with alumina berl saddles while the bottom 4 in. contained catalyst dispersed in granular glass. The catalyst used was 20/40 mesh, lanthanum exchanged, Y-type molecular sieve steamed for 24 hr to increase stability. Reagent-grade cumene was fed by a syringe pump to the top of the reactor where it was vaporized, preheated, and passed through the catalyst zone in a gaseous state. Cumene and benzene were condensed out of the hot reactor effluent and collected as a liquid in a dropout pot at the bottom of the reactor. Propylene was collected by the downward displacement of water in gas burettes. Both the liquid and

* Space time is the inverse of space velocity.

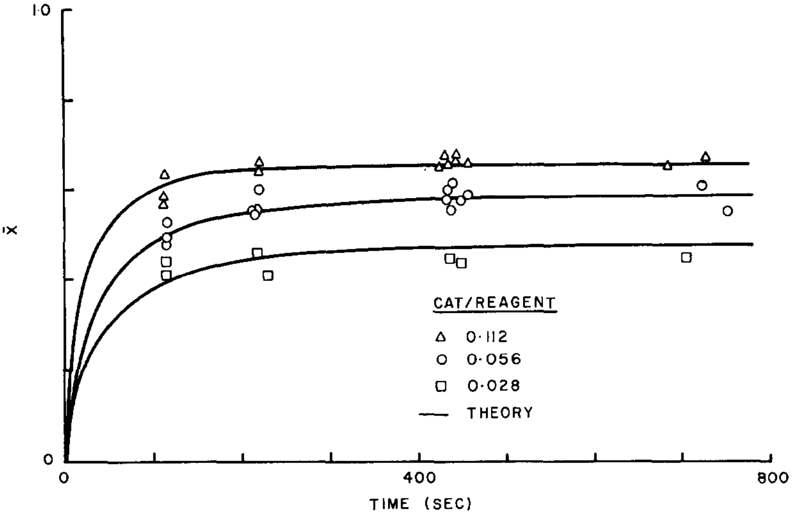

FIG. 2. Best fit of the 400°C experimental data with the theoretical model.

gaseous products were analyzed by gas chromatography.

An experimental run involved pumping a measured volume of liquid at a constant rate (τ) over a given weight of catalyst and measuring the total run time (t_f). The liquid product collected during the run was analyzed to obtain a measure of the average or integral conversion ($\bar{x}$). Experimental runs were performed at three nominal reaction temperatures: 400, 450, and 500°C. The catalyst-to-reagent ratio (P) was changed by packing reactors with various weights of catalyst, and keeping the weight of cumene feed per run the same throughout the experimental program. At each temperature data were collected as three catalyst/reagent ratios. Runs were randomized with respect to temperature and catalyst/reagent ratio in order to avoid trends in the experimental data.

The blank reaction under the reported experimental conditions was zero in all cases.

CORRELATION OF RESULTS

There is consistent evidence (see Figs. 2, 3, and 4) that the catalyst used in this

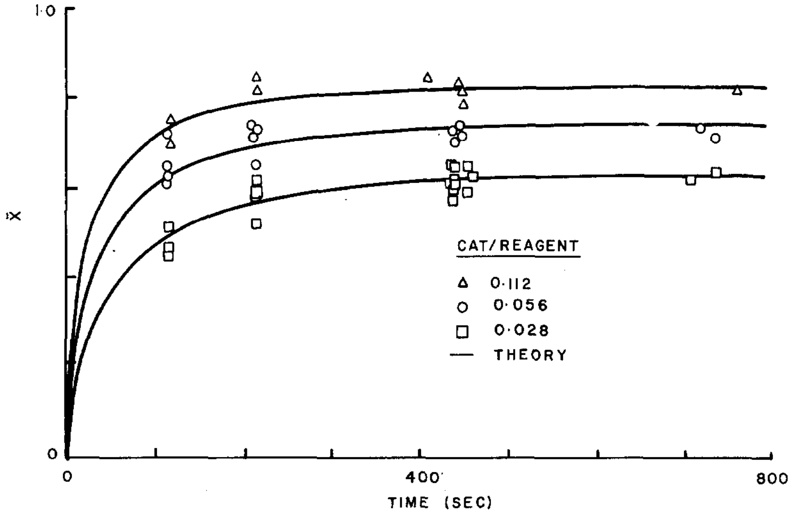

FIG. 3. Best fit of the 450°C experimental data with the theoretical model.

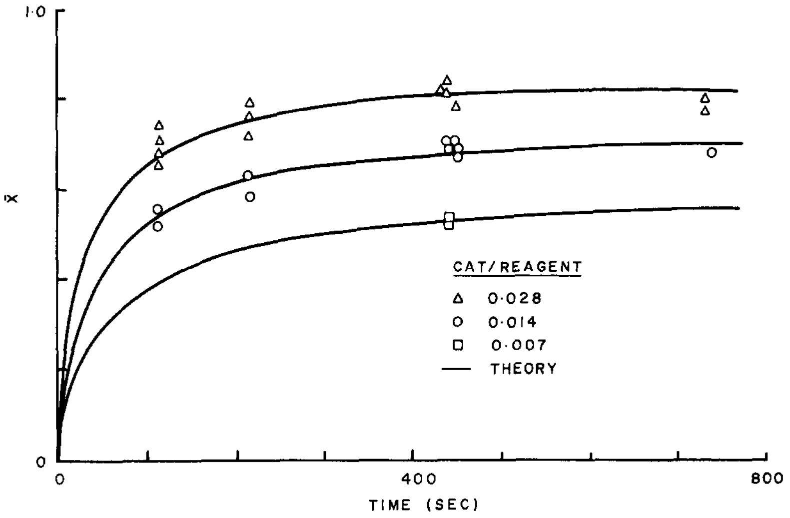

FIG. 4. Best fit of the 500°C experimental data with the theoretical model.

study displayed class II catalyst aging behavior (*1*, *2*) over the entire experimental region tested. Class II catalysts are characterized mathematically by an aging exponent of 1.0. Thus the aging exponent, N, was set at 1.0 throughout the correlation of the data. This resulted in a reduction of the complexity of the model by eliminating one of the parameters.

The estimation of the values of the parameters G, p', and s' was accomplished by a gradient method using a computer. The sum of squares of the residuals (SSR) was employed as a criterion of the goodness of fit.

The experimental results obtained at each nominal reaction temperature were correlated separately. The optimum values of the parameters, G, p', and s' at each nominal reaction temperature are presented in Table 1. Theoretical curves obtained using the constants in Table 1 are shown in Figs. 2, 3, and 4 together with the experimental results.

DISCUSSION

The Aging Parameters

The significance of $N = 1.0$ or class II catalyst aging behavior can be displayed by writing N in terms of m, the number of sites involved in a deactivating event, and n, the order of the catalytic reaction with respect to the concentration of active sites (*2*)

$$N = n/(m - 1). \qquad (8)$$

It is generally accepted that the cracking of cumene occurs with the chemisorption of cumene on a single active site. Corrigan *et al.* (*3*) in their analysis used models based on both single-site and dual-site mechanisms to correlate their experimental results. They concluded as a result of this effort that the reaction proceeded according to the single-site mechanism. Recent authors (*4–6*) also subscribe to this hypothesis. If we accept $n = 1$ for this reaction then $m = 2$, suggesting that 2 sites are removed for each deactivating event.

TABLE 1
THE OPTIMUM VALUES OF G, p', s', AND q'

Temp (°C)	G (sec^{-1})	p' (sec)	s' (sec)	q' (sec)
400	0.020	1.01×10^{-2}	1.19×10^{-3}	1.13×10^{-2}
450	0.013	1.09×10^{-2}	1.04×10^{-3}	1.19×10^{-2}
500	0.013	5.67×10^{-3}	3.38×10^{-4}	6.10×10^{-3}

On the basis of an observed shortage of propylene in the reaction products it is postulated that propylene is the main reactant in the formation of coke on the catalyst. Voge (*7*) and Appleby (*8*) both state that condensation reactions, in which aromatics and olefins form carbon–carbon bonds, result in the formation of coke. Such polymerization reactions on solids have been investigated for several olefins including propylene by Thomas (*9*). It was found that, using a silica–alumina cracking catalyst and a propane-propylene mixture containing 18% propylene, some propylene was polymerized at temperatures as low as 250 to 300°C at an elevated pressure. Thomas also noted a very rapid decline in the catalyst activity accompanying this reaction.

On the basis of the above evidence we propose that catalyst decay in this reaction is caused primarily by the dimerization of propyl particles on the surface followed by dehydrogenation.

The second aging parameter, the aging constant G, has been correlated as a function of temperature as follows: (see Fig. 5)

$$G = 2.78 \times 10^{-3} e^{2.4 \times 10^3/RT}.$$

The positive slope of this Arrhenius expression indicates that the aging reaction is more rapid at lower temperatures. Now, the aging constant, G, can be written in the form

$$G = (m - 1)k_d[S_0]^{m-1}[I], \qquad (9)$$

where [I] is the concentration of poisons in the environment of the catalyst. The terms $(m - 1)$ and $[S_0]^{m-1}$ are independent of temperature. The terms k_d and [I] on the other hand are both functions of temperature. Thus k_d contains the activation energy of the aging reaction while [I] represents a measure of the concentration of poisoning complexes chemisorbed on the catalyst surface. If aging occurs by a Hinshelwood mechanism as suggested above, [I] can be written as a function of the fraction of active sites covered by propylene.

$$[I] \alpha \theta_p^2 = \left(\frac{K_p[P]}{1 + K_c[C] + K_p[P] + K_b[B]} \right)^2, \qquad (10)$$

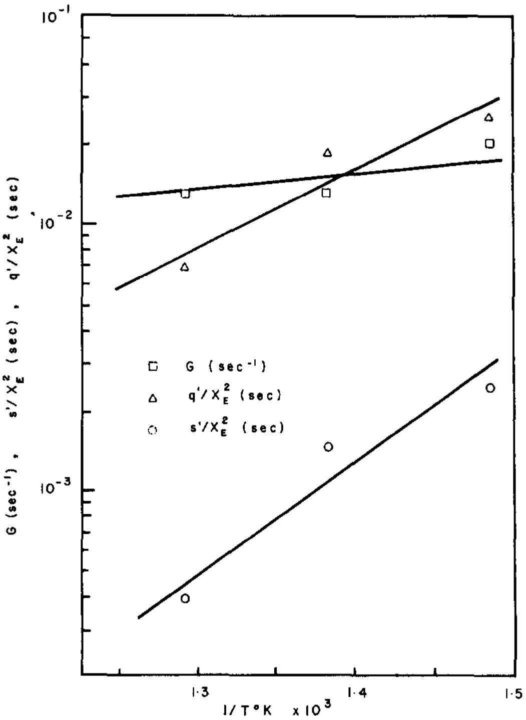

FIG. 5. Temperature correlation of G, q'/X_E^2, s'/X_E^2.

where θ_p is the fraction of sites covered by propylene.

K_c, K_p, K_b are the adsorption equilibrium constants for cumene, propylene, and benzene, respectively, and C, P, and B are cumene, propylene, and benzene, respectively. Thus the concentration of the poison [I] is a function of the temperature-dependent adsorption-equilibrium constants of cumene, benzene, and propylene. The combination of the activation energy of the aging reaction and the heats of adsorption involved in [I] could produce the observed slope of the Arrhenius plot of G vs $1/T$. Unfortunately, we are unable to be more specific in regard to the mechanism of the decay reaction at this time. We prefer to think of G as a "garbage parameter" and will avoid mechanistic interpretations of its significance.

The Reaction Parameters

The parameter, s', which has the form

$$s' = \frac{(K_c + 1)x_e^2}{k_2[S_0]K_c} \text{ (when } [C_0] = 1 \text{ atm)} \qquad (11)$$

can be rearranged as follows:

$$\frac{s'}{x_e^2} = \frac{1}{k_2[\mathrm{S}_0]} + \frac{1}{k_2[\mathrm{S}_0]K_c}. \qquad (12)$$

The modified parameter s'/x_e^2 is the sum of two exponential terms. Only two shapes of Arrhenius plots can result from the sum of two such exponentials: If the terms are of the same magnitude and of different slopes an upward concave curve will result; in all other cases a straight line correlation will be observed.

A similar modification of the parameter, p', gives

$$\frac{p'}{x_e^2} = \frac{K_y}{k_2[\mathrm{S}_0]K_c} + \frac{K_z}{k_2[\mathrm{S}_0]K_c} - \frac{1}{k_2[\mathrm{S}_0]} + \frac{1}{k_2[\mathrm{S}_0]K_c}. \qquad (13)$$

The parameter p'/x_e^2 consists of four exponential terms, one of which is negative. An Arrhenius plot of such a combination of exponentials can result in several forms depending on the relative size of each term. The problem can be simplified as follows: A parameter q' which can be calculated from the relationship (1)

$$q' = p' + s' \qquad (14)$$

can be put in the form

$$\frac{q'}{x_e^2} = \frac{K_y}{k_2[\mathrm{S}_0]K_c} + \frac{K_z}{k_2[\mathrm{S}_0]K_c} + \frac{2}{k_2[\mathrm{S}_0]K_c}. \qquad (15)$$

Here we have the sum of three exponential terms. An Arrhenius plot of q'/x_e^2 vs $1/T$°K takes the form of a straight line if one term is much greater than the others or if the dominant terms have the same slope. If the dominant exponential terms do not have the same slope then an upward concave correlation curve results.

Arrhenius plots of s'/x_e^2 and q'/x_e^2 against $1/T$ using the data of Table 1 are shown in Fig. 5. In both cases the values of s'/x_e^2 and q'/x_e^2 appear to fit a straight line rather than correlation curves which are concave upward. Linear least squares regression analysis of each set of data points yields

$$\frac{s'}{x_e^2} = 1.411 \times 10^{-9} e^{19.5\times10^3/RT} \qquad (16)$$

and

$$\frac{q'}{x_e^2} = 1.208 \times 10^{-6} e^{13.5\times10^3/RT}. \qquad (17)$$

The sum of the two exponential terms of the parameter s'/x_e^2 can result in a linear Arrhenius type correlation only if both terms have the same slope or if one term is much larger than the other. The first case is unlikely since $1/k_2\ [\mathrm{S}_0]$ has a slope of E_2/R while $1/k_2\ [\mathrm{S}_0]K_c$ has a slope of $(E_2 - E_c)/R$. The heat of adsorption of cumene, E_c, has been estimated from cumene cracking studies on several types of catalysts to be in range of 6 to 22 kcal/mole (*4*, *6*, *10*). This suggests that there would be a significant difference between, E_2/R and $(E_2 - E_c)/R$. The alternative explanation, that one term is larger than the other, is, therefore, more probable.

It can be shown that if the second term in Eq. (12) is accepted as the dominant term we are led by use of Eqs. (12) and (15) to the conclusion that the heat of adsorption of Y or Z is negative. Thus the only viable conclusion is that

$$\frac{s'}{x_e^2} = \frac{1}{k_2[\mathrm{S}_0]} = 1.411 \times 10^{-9} e^{19.5\times10^3/RT} \qquad (18)$$

and hence

$$k_2[\mathrm{S}_0] = 7.09 \times 10^{8} e^{-19.5\times10^2/RT}. \qquad (19)$$

If we assign the activation energy of 19.5 kcal/mole to k_2 we find ourselves in fair agreement with a number of previously reported values for the activation energy for cumene cracking as shown in Table 2.

TABLE 2

THE EXPERIMENTAL ACTIVATION ENERGIES OF k_2

Source	Catalyst	E_2 kcal/gmole
Prater and Lago (*11*)	Silica–alumina (10% alumina)	40.0
Pansing and Malloy (*10*)	Silica–alumina (cogelled)	20.6
Maatman *et al.* (*6*)	Silica–alumina (12.4% alumina) (cogelled)	23.6
Horton and Maatman (*4*)	Silica–alumina (10% alumina) (cogelled)	23.4
Present study	Synthetic silica–alumina molecular sieve	19.5

This, however, turns out to be an unhappy coincidence.

When the ΔE of the reaction

$$\text{cumene} \longrightarrow \text{benzene} + \text{propylene}$$

is calculated (*12*) it is found that the overall ΔE at ~500°C is ~21 kcal/mole. This in turn can mean one of two things. Either the heat of adsorption of cumene is negative (an endothermic reaction) or the catalyst used is diffusion limited.

We ascertained that our catalyst was not diffusion limited in the particles by testing particles of various sizes until a size was found which upon further reduction did not result in a change in the rate of reaction. There remains the possibility that the catalyst is diffusion limited in its crystallites. That is now the suspected cause of the low activation energy.

Fortunately we know from previous work (*13*) that the mechanism of decay is not influenced by diffusion limitations, and we can, therefore, state with some assurance that decay proceeds by simultaneous loss of two active sites. Due to the results reported above we are presently undertaking an experimental study of the diffusion effects in the crystallites of La–Y catalysts.

CONCLUSIONS

Our newly developed model of the catalytic cracking of cumene in a fixed-bed reactor was applied to experimental data. Although our mechanism is consistent with previous mechanisms for this reaction, it is more comprehensive and includes the reverse alkylation reaction and the adsorption of all components of the reaction on the catalyst surface. The model also takes into account catalyst aging, volume expansion, and chemical equilibrium. Experimental data obtained over a wide range of conditions were successfully correlated with this model.

Wojciechowski's time-on-stream theory of catalyst decay was incorporated into the theoretical model to account for the aging of the catalyst. The success of the model in correlating experimental data leads to the conclusion that the time-on-stream theory of catalyst decay adequately represents the actual aging behavior in the example reported here. Since the catalyst used in this study displayed class II aging behavior over the entire range of experimental conditions, it is argued that two active sites on the catalyst are removed for each deactivating event. This in turn suggests that the aging of the catalyst may occur by the reaction of two adsorbed species by a Hinshelwood mechanism. It is also postulated that propylene is the primary reactant in the formation of coke on the catalyst and that this coke, deposited on active sites, results in the observed loss of activity during use. No evidence was uncovered to indicate the presence of steady-state adsorption of poisons on the catalyst surface. It was previously postulated by other authors that this phenomenon resulted in the pseudo-steady state of catalyst activity reported on other catalysts.

The rate of catalyst aging appears to be inversely correlated with the reaction temperature as well as being a function of time. At 400°C, the rate of decay is more rapid than at the higher reaction temperatures. Unfortunately the activation energy found for the cracking reaction is too low and we suspect that the catalyst is diffusion limited in the crystallites.

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