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Kinetics of Reaction and Deactivation: Cumene Disproportionation on a Commercial Hydrocracking Catalyst

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Cumene disproportionation has been utilized as a probe reaction to study the acidic function of a hydrocracking catalyst. Differential rate data obtained in a fixed-bed microreactor at total pressures near 8 atm and temperatures ranging from 428 to 455°K have been extrapolated to time zero by two different techniques in order to offset effects of slow catalyst deactivation during the experiments. The resultant initial rate data have been shown to be consistent with a Langmuir–Hinshelwood reaction model involving two adjacently adsorbed cumene molecules.

INTRODUCTION

We have recently reported a series of studies conducted in this laboratory to investigate the fate of the hydrogenation function of a typical commercial hydrocracking catalyst upon deactivation (*1*). Cyclohexene hydrogenation was used as the probe reaction for the Co—Mo function after the acidic function was prepoisoned with NH_3. In the present paper we report initial results of a complementary investigation of the acidic function using cumene disproportionation as probe reaction.

Several interesting and interrelated problems arise in using such a reaction for characterization of the acidic function. One might ask first whether this disproportionation reaction is a feasible one for such an objective. Active acidic catalysts readily deactivate, and there are possible correlations between such deactivation and the determination of the kinetic parameters used for characterization. Since the disproportionation activity decreases with time-on-stream in experiments with any given catalyst sample, the associated kinetic parameters must be determined using initial rate data. This requires extrapolation to zero time-on-stream for set conditions, and it is not at all clear what effect the extrapolation procedure has on kinetic evaluations. These interrelated problems are addressed herein. The results presented in this paper refer only to studies of the fresh catalyst and the catalyst support. Corresponding studies of samples deactivated for various periods of time under commercial operation, and of regenerated catalysts, will be presented subsequently.

A central question in the analysis of disproportionation data is the relation of activity to time-on-stream or other parameters of the deactivation process. An exponential correlation:

$$a(t) = \exp(-\alpha t) \tag{1}$$

where $a(t)$ is the catalytic activity at time-on-stream t, has been used extensively in detailing the deactivation of FCC catalysts by Weekman and co-workers (*2–5*) and has been applied in more detail to other reactions in more recent work by Corella and co-workers (*6, 7*). Corma and Wojciechowski (*8*) have proposed a hyperbolic correlation for deactivation of LaY zeolites in cumene cracking:

$$a(t) = (1 + \beta t)^{-1} \tag{2}$$

Finally, there is the father of all deactivation correlations, that of Voorhies (*9*), which in its original form proposed that:

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$$C_c = bt^n \quad (3)$$

where C_c is the amount of coke deposited on the catalyst and b and n are empirical constants. In the original and subsequent work, n was found often to be in the vicinity of 0.5. This form of correlation, of course, requires separate information on the relationship between C_c and $a(t)$. Mahoney (*10*) proposed the following modification, based on a combination of concepts and experience with Eqs. (1) and (3), for deactivation of Pt/Al_2O_3 in *n*-heptane reforming:

$$x(t) = x(0)\exp(-\gamma t^{0.5}) \quad (4)$$

This, which we will refer to as a "Voorhies type" correlation, has also been employed successfully in our prior work (*11*) with cyclohexene hydrogenation on Co-Mo hydrocracking catalysts.

SCOPE

As stated above, a primary purpose of the present work is to investigate cumene disproportionation as a probe reaction for characterization of acidic function catalysis. We do this primarily via the device of kinetic correlation, which in turn involves some delicate considerations as to interactions with deactivation. Kinetics are suggestive, though not definitive of reaction mechanism; we present a discussion of the mechanism of alkylbenzene disproportionation since there appear to be some inconsistencies in the proposals of other workers. Finally, we address the question of how the form of the rate expression and the estimates of kinetic parameters are affected by the decay correlation employed, and the fundamental significance of such correlations.

EXPERIMENTAL

A conventional once-through flow reactor, operated normally at conversions below 16%, was used for experiments at a hydrogen partial pressure of 7.6 atm with cumene partial pressures ranging from 0.076 to 0.724 atm and at reaction temperatures ranging from 428 to 455°K. Space velocities were in the range of 1.87 to 9.60 h^{-1} in these experiments; conversion as a function of time-on-stream was determined via on line gas chromatography with 10 to 12 samples typically analyzed during a 4- to 6-h experiment. Products measured were C_3's, benzene, toluene, C_8-aromatics, cumene, and isomers of ethylisopropyl-, triisopropyl-, and diisopropylbenzene. Experiments were run under conditions such that diffusional and thermodynamic limitations were absent (*12*).

The fresh hydrocracking catalyst and the acidic support were supplied by Amoco Oil Company. This material is a typical commercial formulation with the Co-Mo function supported on a crystalline aluminosilicate suspended in an amorphous SiO_2/Al_2O_3 matrix. In the experiments reported here, all samples were crushed and screened to 0.2 mm average particle size and pretreated before reaction as follows: N_2, 25°C, 1 h; N_2, 365°C, 1 h; N_2, 25°C, 1 h. Reagent cumene (Aldrich Chemical, 99%) was further purified by passage through a column of SiO_2 to remove cumene hydroperoxide and was stored under hydrogen prior to use. Further experimental details are given by Absil (*12*).

RESULTS

Product Distributions

The product distributions for cumene hydrocracking on the fresh catalyst with and without metals were examined as a function of time-on-stream and reaction temperature. Comparison of the various distributions indicated that:

(i) The hydrogenation function exhibited negligible activity at a hydrogen partial pressure of 7.6 atm and at reaction temperatures less than 680°K.

(ii) Cumene cracking and disproportionation were competitive reactions; the extent of cracking increased with increasing reaction temperature as illustrated in Fig. 1.

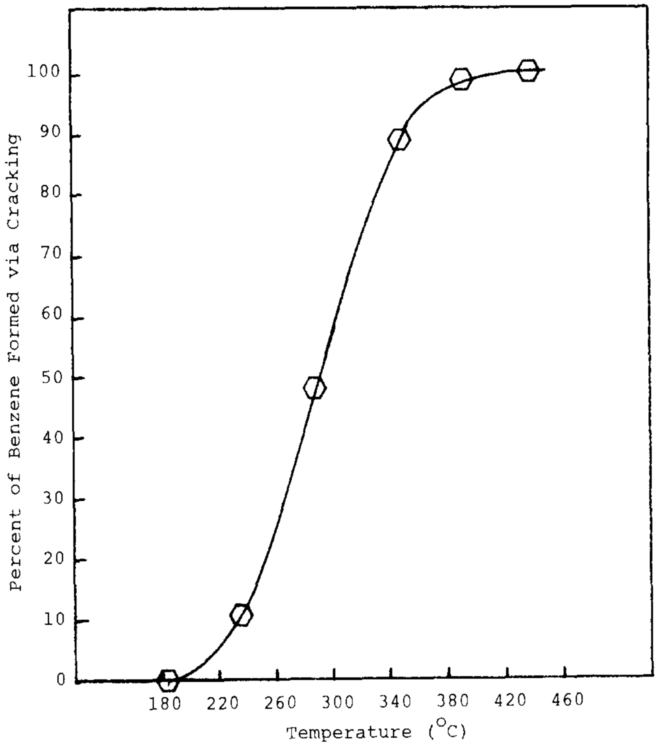

FIG. 1. Cumene disproportionation versus cumene cracking as a function of reaction temperature on a fresh catalyst deactivated to a steady state at 455°K, cumene partial pressure of 0.137 atm, and space velocity of 7.79 h^{-1}.

(iii) At the reaction conditions under which the kinetic experiments were performed cumene disproportionation was the predominant reaction; cumene cracking was of importance only during the first 120 min on stream. Other reactions leading to the formation of toluene, C_8-aromatics, ethylisopropyl- and triisopropylbenzene occurred, but to a negligible extent.

KINETICS OF CUMENE DISPROPORTIONATION

Analysis via the Voorhies Type Correlation

The experimental conversion versus time-on-stream data were correlated to the initial rate of benzene formation due to disproportionation, $r_b'(0)$, using Eq. (4) via:

$$\begin{aligned}&\text{(i) } x_2'(t) = x_2(t) - x_3(t)\\&\text{(ii) } x_2'(t) = x_2'(0)\exp(-\gamma t^{0.5}) \qquad (5)\\&\text{(iii) } r_b'(0) = (F/W)x_2'(0)\end{aligned}$$

where:

$x_2(t)$ = the fraction of cumene converted to benzene,

$x_3(t)$ = the fraction of cumene converted to C_3's,

$x_2'(t)$ = the fraction of cumene converted to benzene via disproportionation, as determined by the Voorhies type correlation.

Typical results are shown in Fig. 2 in terms of ln x_2' versus $t^{0.5}$. The linear plot corresponds well to the deactivation model. Reproducibility experiments indicated a 90% confidence interval of ±15% to the data on $r_b'(0)$ as tabulated in Table 1. The kinetic analysis of these data (*12*) resulted in best fit to the following Langmuir–Hinshelwood expression:

$$r_b'(0) = \frac{k_2K_2^2P_C^2}{(1 + K_2P_C)^2} \qquad (6)$$

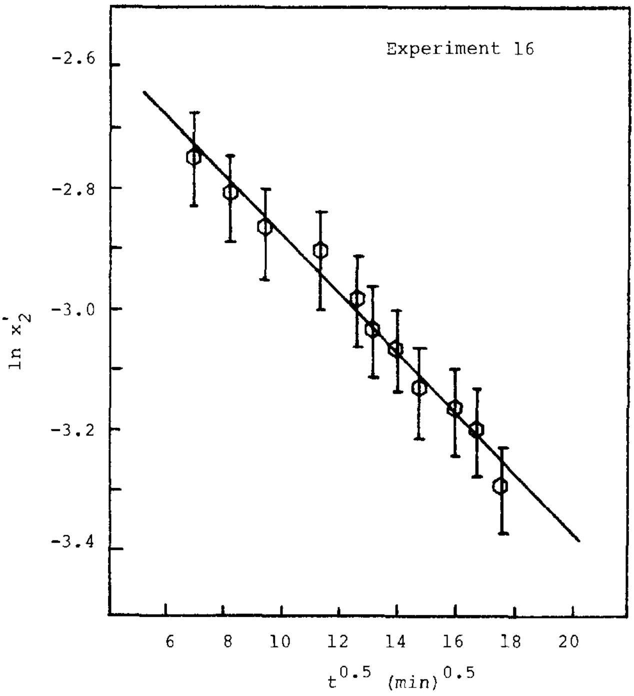

FIG. 2. Plot of Voorhies type correlation for cumene disproportionation on the fresh hydrocracking catalyst at 443°K, cumene partial pressure of 0.6393 atm, and space velocity of 4.65 h^{-1}. $\gamma = 4.82 \times 10^{-2}$ $min^{-0.5}$.

TABLE 1

Initial Rate Data for Cumene Disproportionation on Fresh Hydrocracking Catalyst as Determined by the Voorhies Type Correlation and the Hyperbolic Correlation

Reaction temperature (°K)	Cumene partial pressure (atm)	g mol/g catalyst/min	
		$r_b'(0) \times 10^5$	$r_b''(0) \times 10^5$
455	0.076	5.26	4.55
455	0.082	6.81	4.68
455	0.137	8.91	6.22
455	0.138	8.04	6.17
455	0.140	8.27	7.27
455	0.145	8.38	6.78
455	0.260	11.03	9.05
455	0.342	14.40	10.97
455	0.633	12.11	9.04
443	0.130	4.31	3.43
443	0.309	5.60	4.54
443	0.639	5.05	4.54
428	0.142	2.80	2.32
428	0.329	2.88	2.42
428	0.718	3.13	2.65

with

$$K_2 = K_2^0\exp(Q_2/RT)$$
$$k_2 = k_2^0\exp(-E/RT)$$

As stated above, hydrogen partial pressure (P_H) was fixed in this series of experiments, hence its effect on kinetics is embedded in the constants of Eq. (6). A simple analysis of this expression suggests $[r_b'(0)]^{-0.5}$ versus P_C^{-1} should be linear; this result is shown in Fig. 3 and the corresponding kinetic parameters determined from unweighted linear least squares regression of the initial rate data in this form are reported in Table 2. The average deviation in the predictions of $[r_b'(0)]^{-0.5}$ using these parameters was less than ±5.7% and the maximum was less than ±13.5%.

Analysis via the Hyperbolic Correlation

Combination of the rate equation (6) with the hyperbolic correlation yields, in linear-

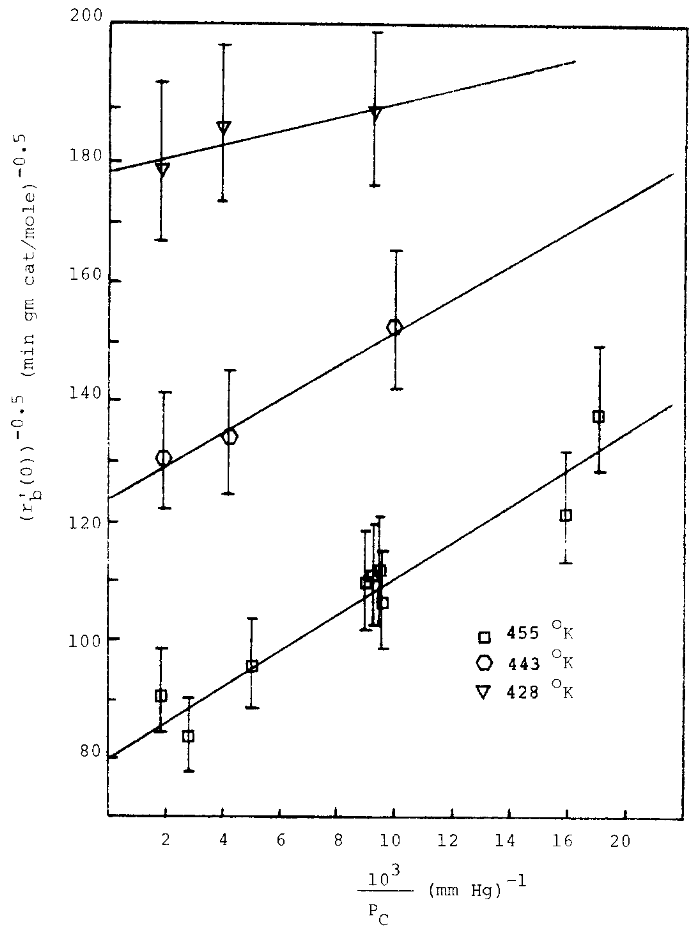

FIG. 3. Plots of $[r_b'(0)^{-0.5}$ versus P_C^{-1} at constant temperature.

ized form:

$$\frac{1}{[x_2''(t)]^{0.5}} = \frac{[1 + \delta t]}{[x_2''(0)]^{0.5}} \qquad (7)$$

Detailed derivation of this equation is given in Appendix A. This form was also applied to analysis of the experimental data. For this case the initial rate of benzene formation from disproportionation, $r_b''(0)$, was determined from Eq. (7), and the following:

$$\begin{aligned} &\text{(i) } x_2''(t) = x_2(t) - x_3(t) \\ &\text{(ii) } r_b''(0) = (F/W)\, x_2''(0) \end{aligned} \qquad (8)$$

where $x_2''(t)$ = the fraction of cumene converted to benzene via disproportionation as determined by the hyperbolic correlation.

The hyperbolic correlation approach also managed to fit the experimental data quite well. A plot of $[x_2''(t)]^{-0.5}$ versus t suggested by Eq. (7) is given in Fig. 4; again good linearity is obtained. Corresponding values of the initial rate from this analysis are also given in Table 1. Reproducibility experi-

TABLE 2

Kinetic Parameters of Cumene Disproportionation on the Fresh Hydrocracking Catalyst

Model parameter	Voorhies type correlation	Hyperbolic correlation
E (kcal/mol)	22.9	20.7
Q_2 (kcal/mol)	25.4	19.7
K_2^0 (atm)$^{-1}$	1.37×10^{-11}	9.44×10^{-9}
k_2 (g mol/g cat/min)	1.24×10^{7}	8.36×10^{5}

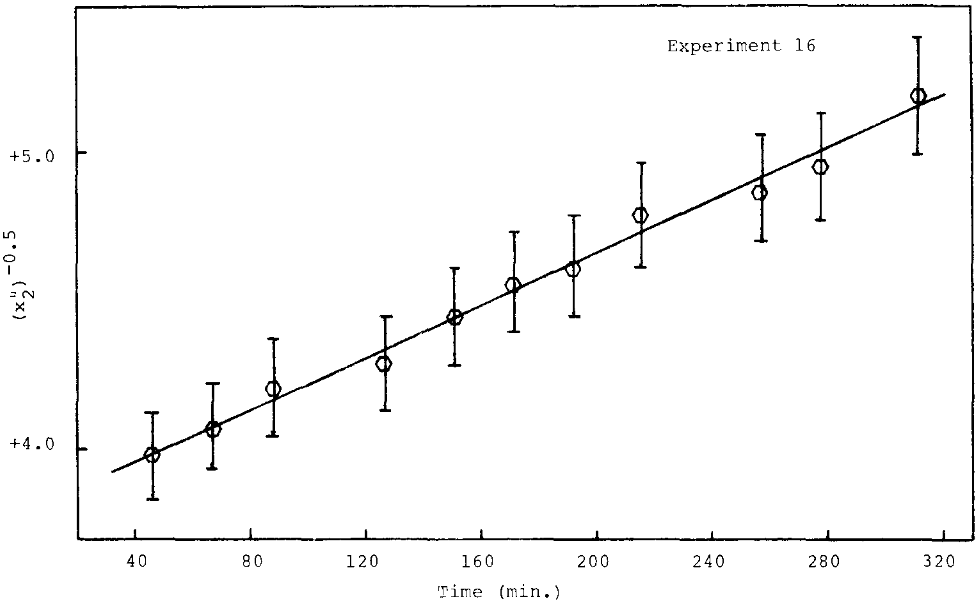

FIG. 4. Plot of Eq. (7) for cumene disproportionation on the fresh hydrocracking catalyst at 443°K, cumene partial pressure of 0.6393 atm, and space velocity of 4.65 h^{-1}. $\beta = 1.17 \times 10^{-3}$ min^{-1}.

ments indicated a 90% confidence interval of ±12% for the $r_0''(0)$ data. These results were also tested according to the linearized form of Eq. (6) and are shown in Fig. 5 with corresponding kinetic parameters listed in Table 2. In this case there was an average deviation of ±5.3% with a maximum of ±12%, which is essentially indistinguishable from the results obtained using the Voorhies type correlation.

DISCUSSION

The Feasibility of Cumene Disproportionation as Probe Reaction

A primary purpose of the present work was to ascertain the feasibility of cumene disproportionation as a probe reaction for characterization of acidic function catalysis. Two affirmative pieces of evidence exist: (i) Catalyst deactivation was slow enough so that extrapolation to zero time-on-stream via two rather different procedures was reliable as indicated by the agreement of the kinetic model with experimental data. (ii) Our best fit kinetic model for cumene disproportionation was the same as those reported for the disproportionation of other alkylbenzenes by Pukanic and Massoth (*13*) and by Gnep and Guisnet (*14*).

Reaction Mechanism For Cumene Disproportionation

Based on the intermolecular transalkylation–alkylation mechanisms proposed by Pines (*15, 16*) and Roberts and Roengsumran (*17*) and on the inhibiting effect of hydrogen on toluene disproportionation reported by Gnep and Guisnet (*14*), we propose the following reaction mechanism for cumene disproportionation. Reaction sequence (*9*) involves two adjacently adsorbed cumene molecules; the symbols are defined in Fig. 6.

$$\begin{array}{llll} \text{(i)} & 2[\mathrm{C} + \mathrm{S} & \rightleftharpoons \mathrm{CS} + \mathrm{H_2}, & L_2] \\ \text{(ii)} & 2\mathrm{CS} + \mathrm{H_2} & \rightarrow \mathrm{I_1S} + \mathrm{S}, & l_2 \\ \text{(iii)} & \mathrm{I_1S} & \rightleftharpoons \mathrm{I} + \mathrm{S} & \\ \text{(iv)} & \mathrm{I} + \mathrm{S} & \rightleftharpoons \mathrm{I_2S} & \\ \text{(v)} & \mathrm{I_2S} & \rightleftharpoons \mathrm{B} + \mathrm{DS} & \\ \text{(vi)} & \mathrm{DS} + \mathrm{H_2} & \rightleftharpoons \mathrm{D} + \mathrm{S} & \end{array} \qquad (9)$$

The cumene adsorption step (i) is well es-

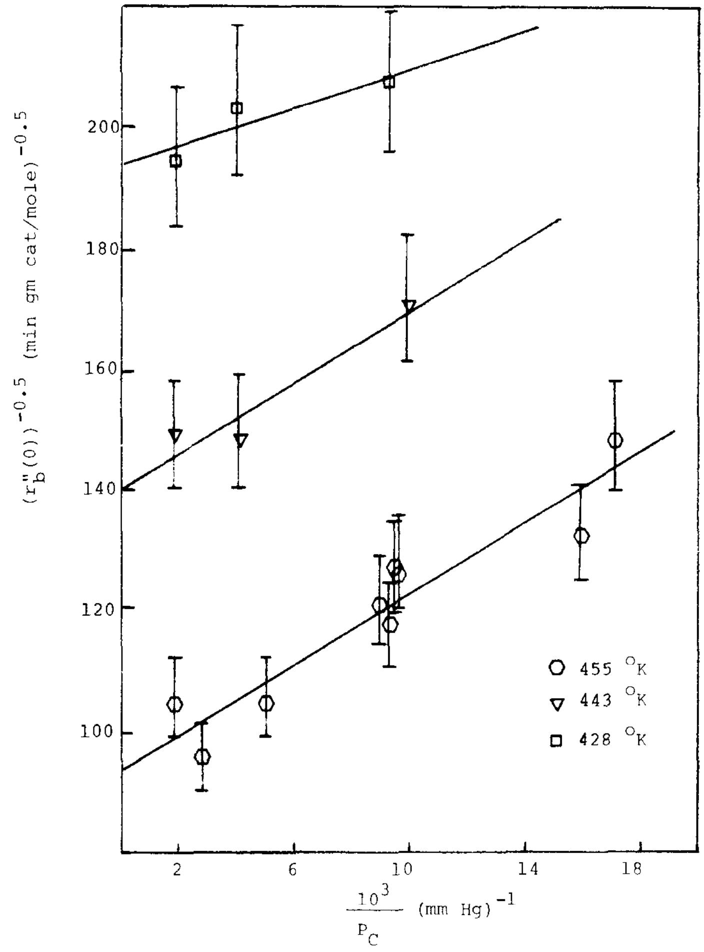

FIG. 5. Plots of $[r''_b(0)]^{-0.5}$ versus P_C^{-1} at constant temperature.

tablished (*14, 16*). Assuming that the rate-determining step is the irreversible surface reaction (ii) and that product inhibition is negligible at low conversions yields

$$r'_b(0) = \frac{l_2 P_H [L_2/P_H]^2 P_C^2}{[1 + (L_2/P_H)P_C]^2} \qquad (10)$$

At a constant hydrogen partial pressure:

$$k_2 = l_2 P_H$$

and

$$K_2 = L_2/P_H \qquad (11)$$

Substitution of these definitions into Eq. (10) yields the rate expression (6). To ascertain the effect of hydrogen on the rate of cumene disproportionation, further kinetic studies at various hydrogen partial pressures will be required.

Other reaction sequences for alkylbenzene disproportionation were considered. In (12) below the adsorbed cumene molecule is attacked by a gas phase molecule (as proposed by Corma and Wojciechowski (*8*)).

$$\begin{array}{lll} \text{(i)}\ C + S \rightleftharpoons CS + H_2, & L_2 & \\ \text{(ii)}\ CS + C \rightarrow I_1S, & l_4 & (12) \\ \quad\vdots & & \end{array}$$

Assuming again that the irreversible surface reaction (ii) is rate-determining and that product inhibition is negligible at low conversions yields:

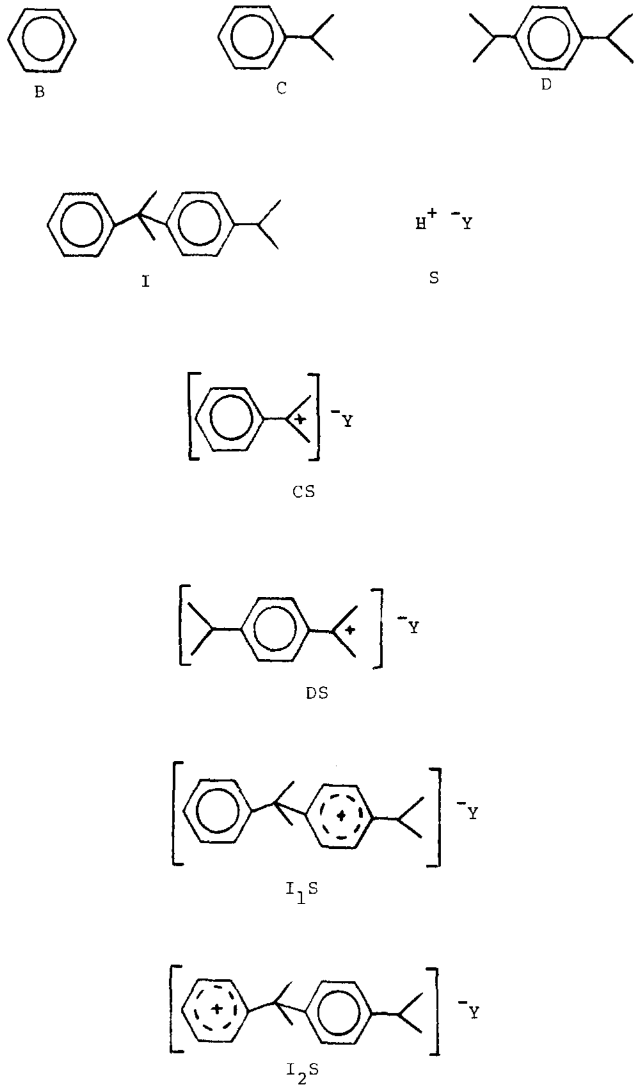

FIG. 6. Legend of symbols used in the various reaction mechanisms.

$$r_b'(0) = \frac{l_4(L_2/P_H)P_C^2}{[1 + (L_2/P_H)P_C]} \qquad (13)$$

Plots of $P_C/r_b'(0)$ versus P_C^{-1} were not only nonlinear, but also yielded negative adsorption equilibrium constants, thus invalidating this model. A similar conclusion was reached by Gnep and Guisnet (*14*) in their study of toluene disproportionation.

In reaction mechanism (*14*) the adsorbed alkylbenzene molecule is attacked by C_1S, a π-adsorbed alkylbenzene molecule (as proposed by Gnep and Guisnet (*14*)).

$$\begin{array}{llll} \text{(i)} & C + S \rightleftharpoons CS + H_2, & L_2 & \\ \text{(ii)} & C + S \rightleftharpoons C_1S, & L_1 & (14) \\ \text{(iii)} & CS + C_1S \rightarrow I_1S + S, & l_3 & \\ & \vdots & & \end{array}$$

Assuming once more that the irreversible surface reaction (iii) is rate-determining and that product inhibition is negligible at low conversions yields:

$$r_b'(0) = \frac{l_3L_1(L_2/P_H)P_C^2}{[1 + (L_1 + L_2/P_H)P_C]^2} \qquad (15)$$

Plots of $[r_b'(0)]^{-0.5}$ versus P_C^{-1} were linear as indicated in Figs. 3 and 5. While it was not possible to determine the individual kinetic and equilibrium parameters of this model from the available data, the group $[l_3L_1L_2]$ would be expected to satisfy the usual Arrhenius form if the model were appropriate. Since a plot of $\ln[l_3L_1L_2/P_H]$ versus $1/T$ was not linear within the expected limits of experimental error for this work, reaction sequence (14) was also rejected.

Thus, mechanism (9) has been retained as our working model for the cumene disproportionation reaction pending additional kinetic studies and/or the application of the investigative techniques of modern surface science to this problem.

Formation of The Coke Precursor

The demise of the disproportionation activity with time-on-stream is ascribed to the neutralization of active acid sites by highly unsaturated cyclic hydrocarbons which act as organic bases (*16*). However, before a reaction for the formation of the coke precursor in the present system can be proposed, the chemical compounds responsible for deactivation must be identified. To determine the origin of coke formation in cumene cracking and disproportionation over amorphous high alumina cracking catalyst, Pansing and Malloy (*18*) performed a series of radioactive tracer experiments in which cumene was labeled in its propyl group with ^{14}C. Since the specific activities of the carbon in the coke and diisopropylbenzene were within 5%, Pansing and Malloy concluded that coke could have formed exclusively from diisopropylbenzene.

By analogy with the reaction mechanism proposed by Ipatieff *et al.* (*19*) for the hydrocyclialkylation of *p*-cymene and of 4-methylcyclohexene (*16*) and the conclusions of Pansing and Malloy (*18*), the reaction scheme in Fig. 7 is proposed for the formation of coke precursor P_1. The latter may react further with diisopropylbenzene or other molecules composed of P_1 units to yield coke.

Significance of The Decay Correlations

Having discussed the kinetics and the reaction sequence for cumene disproportion-

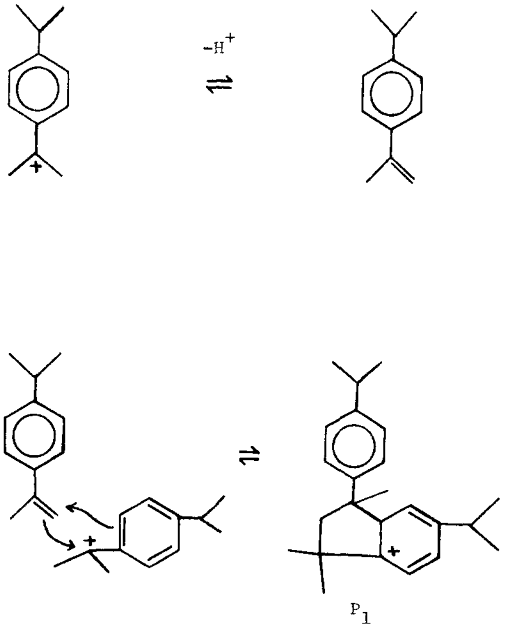

FIG. 7. Reaction for the formation of coke precursor P_1.

ation and the formation of the coke precursor, it is appropriate now to address the question of how the form of the rate expression and the estimates of the kinetic parameters are affected by the decay correlation employed. Indeed, the form of the rate expression appears to be independent of the decay correlation used, since initial rate data determined using either correlation fit the same kinetic model equally well. The data in Table 2, however, reveal that the kinetic parameters as determined by unweighted linear least squares regression of the rearranged linear form of rate equation (6) *are* affected by the type of decay correlation used. The estimates of the activation energies and heats of adsorption are similar, while those of the preexponential factors differ by an order of magnitude. Application of nonlinear least squares regression methods may under some circumstances yield different estimates of these kinetic parameters. Further analysis of these results will be reported in the near future.

Finally, let us consider the fundamental significance of the decay correlations. Since no fundamentally based derivation has yet been presented for the Voorhies type correlation shown in Eq. (4), it must be regarded as purely empirical.

While the hyperbolic correlation can be derived from Wojciechowski's time-on-stream theory (*20*), it too must be treated as an empirical correlation since the theory does not take into account the role of coke precursors in coke formation; i.e., deactivation is assumed to be concentration-independent. Consequently, the time-on-stream theory will predict uniform deactivation in an integral reactor (*21*), even though it is known that concentration gradients are generally present and coke content of the catalyst varies with distance in the reactor (*22*). Wojciechowski (*20*), Best and Wojciechowski (*23*), and Corma and Wojciechowski (*8*) employed this theory to model the deactivation of LaY zeolites in cumene cracking in an integral reactor. Since these works involved complicated kinetic models, any inconsistencies attributed to assuming concentration-independent deactivation, may be buried by the parameterization required. An alternative derivation of the hyperbolic correlation presented in Appendix A demonstrates that it can be used to model separable deactivation by site coverage in differential reactors. In separable deactivation only the number of catalytically active sites decreases with time while their chemical nature remains unchanged. Since the concept of separability is correct only for an ideal surface comprised of sites which all have the same properties and catalytic activity (*24*), and the hyperbolic correlation fit the conversion versus time-on-stream data very well, the behavior of the acidic surface after the first 30 min on stream might well approximate that of an ideal surface. However, since the acidic surface is expected to be initially heterogeneous and nonideal, the surface must be undergoing modification during the deactivation process. Several factors may be responsible for this phenomenon including the preferential deactivation of the most active sites, which will leave the surface progressively less heterogeneous; i.e., more ideal.

While the assumption of a varying distribution of catalytic site activities is not entirely consistent with the postulate of a Langmuir–Hinshelwood kinetic model with fixed parameters, it has often been observed that such models do indeed provide good fits to experimental rate data for catalysts with nonideal surfaces. One must, of course, then be cautious in the interpretation of the values of the parameters and their relationship to those measured in adsorption equilibrium studies. Nonetheless, the potential utility of such an approach is clear.

Similarly, while the agreement of the catalyst deactivation data with the hyperbolic correlation is satisfying, that alone cannot be taken as proof of the proposed mechanism nor rule out the existence of other, perhaps more appropriate models. Indeed, it is entirely possible that a mechanistically inappropriate model might also agree with available data over some restricted range of conditions.

In view of these factors, we offer the reaction mechanism and the present justification of the hyperbolic correlation as useful guides and suggestive models without precluding the possibility that other approaches might prove equally useful or even superior in some circumstances.

As suggested earlier, our intention is to utilize the cumene disproportionation reaction as a probe for characterizing a series of catalysts deactivated to varying degrees. We assume that correction of the experimental reaction rate data for additional activity loss suffered during these studies by means of the hyperbolic or Voorhies type correlation will not introduce any changes in the truc relative merits of the catalysts to be studied. Future studies will permit a test of this assumption.

CONCLUSIONS

(i) Cumene disproportionation is a feasible probe reaction for characterization of acidic function catalysis because deactivation is slow enough to permit accurate extrapolation to zero time-on-stream.

(ii) The kinetic model suggests that cumene disproportionation proceeds via a Langmuir–Hinshelwood type reaction sequence involving two adjacently adsorbed cumene molecules.

(iii) Although the form of the rate expression is independent of the decay correlation employed, the estimates of the kinetic parameters from its linearized form are not.

APPENDIX A

Assuming that the surface reaction is the rate-determining step and neglecting the reverse reaction and product inhibition, a Hougen–Watson analysis of reaction sequence (9) yields

$$\begin{aligned} r''_{\mathrm{b}}(t) &= \frac{k'_2 K_2{}^2 P_{\mathrm{C}}{}^2}{[1 + K_2 P_{\mathrm{C}}]^2}\,[n_{\mathrm{s}}(t)]^2 \qquad \text{(A-1)} \\ &= f(P_{\mathrm{C}}, K_2, k'_2)[n_{\mathrm{s}}(t)]^2 \end{aligned}$$

Separable deactivation has been assumed. In a differential reactor, operated under conditions at which diffusional limitations are absent, the gas composition is uniform. Consequently, $f(P_{\mathrm{C}}, K_2, k'_2)$ is constant throughout the bed and

$$\frac{r''_{\mathrm{b}}(t)}{r''_{\mathrm{b}}(0)} = \frac{x''_2(t)}{x''_2(0)} = \left\{\frac{n_{\mathrm{s}}(t)}{n_{\mathrm{s}}(0)}\right\}^2 \qquad \text{(A-2)}$$

A balance on the number of sites active for cumene disproportionation at time-on-stream t yields:

$$n_{\mathrm{s}}(t) = n_{\mathrm{s}}(0) - n_{\mathrm{s,d}}(t) \qquad \text{(A-3)}$$

where $n_{\mathrm{s,d}}(t)$ are the number of sites active initially but which at time-on-stream t are (i) inactive because of site coverage by coke, (ii) inaccessible because of pore blockage, or (iii) inactive because of isolation. The latter is only of importance for a reaction mechanism involving a surface reaction between two adjacently adsorbed molecules. However, when the coke precursor is deposited in a random way and when coke levels are low, this contribution to $n_{\mathrm{s,d}}$ can be neglected. Thus:

$$n_{\mathrm{s,d}}(t) = [1 - \phi(t)]n_{\mathrm{s}}(0) \qquad \text{(A-4)}$$

where $\phi(t)$ is the probability of finding a site active, i.e., not covered nor blocked, at time-on-stream t (*25*). Beeckman and Froment (*25*) defined $\phi(t)$ as:

$$\phi(t) = P(t)S(t) \qquad \text{(A-5)}$$

where $P(t)$ is the probability that the site is accessible at time t and $S(t)$ is the conditional probability that the site is not covered. They assumed in their derivation that the growth of the coke molecule is infinitely faster than the rate of precursor formation. Under these conditions, pore blockage is, indeed, expected. However, if the rate of growth of the coke molecule is assumed to be negligible compared to the rate of precursor formation, the probability of finding the site accessible is 1.

Thus

$$\phi(t) = S(t) \tag{A-6}$$

In other words, $S(t)$ is the fraction of sites active, and $n_{s,d}(t)$ is the number of sites covered with coke precursor. Assuming that the main reaction and coke formation occur on the same acid sites, $dn_{s,d}(t)/dt$ can be defined as done by Beeckman and Froment (*25*):

$$\frac{d}{dt}\left\{\frac{n_{s,d}(t)}{n_s(0)}\right\} = g(P_i, L_i, l_d)n_s(0)^{n_c-1}\left\{\frac{n_s(t)}{n_s(0)}\right\}^{n_c} \tag{A-7}$$

In a differential bed reactor, operated under conditions at which diffusional limitations are absent, the gas composition is uniform and $g(P_i, L_i, l_d)$ and $n_s(0)^{(n_c-1)}$ can be treated as a constant. Thus:

$$\frac{d}{dt}\left\{\frac{n_{s,d}(t)}{n_s(0)}\right\} = \beta\left\{\frac{n_s(t)}{n_s(0)}\right\}^{n_c} \tag{A-8}$$

Differentiating Eq. (A-3) and substituting Eq. (A-8) in the resulting equation yields

$$\frac{d}{dt}\left\{\frac{n_s(t)}{n_s(0)}\right\} = -\beta\left\{\frac{n_s(t)}{n_s(0)}\right\}^{n_c} \tag{A-9}$$

Upon integration:

$$n_c = 1 \quad \left\{\frac{n_s(t)}{n_s(0)}\right\} = \exp[-\beta t] \tag{A-10}$$

$$n_c \neq 1 \quad \left\{\frac{n_s(t)}{n_s(0)}\right\} = [1 + (n_c - 1)\beta t]^{1-n_c}$$

For $n_c = 2$,

$$\left\{\frac{n_s(t)}{n_s(0)}\right\} = [1 + \beta t]^{-1} \tag{A-11}$$

Substituting Eq. (A-11) in (A-2) and rearranging the resulting equation yields

$$\frac{1}{[x_2''(t)]^{0.5}} = \frac{1}{[x_2''(0)]^{0.5}}[1 + \beta t] \tag{A-12}$$

Equation (A-11) is referred to as the hyperbolic correlation.

NOMENCLATURE

$a(t)$	catalytic activity at time-on-stream t
b	empirical constant used in equation (3)
C_c	coke on catalyst
E	activation energy, kcal/mol
$f(\ )$	function defined in Eq. (A-1)
F	cumene molar flow rate
$g(\ )$	function defined in Eq. (A-7)
k_2	$l_2 P_H$
k_2^0	$l_2^0 P_H$
k_2'	$k_2 [n_s(t)]^{-2}$
K_2	$L_2 [P_H]^{-1}$
K_2^0	$L_2^0 [P_H]^{-1}$
l_2, l_3, l_4	rate constants defined in reaction mechanisms (9), (12), (14)
l_d	rate constant for the formation of the coke precursor
L_1, L_2	adsorption equilibrium constants defined in reaction mechanisms (9), (12), and (14)
n	empirical constant used in Eq (3)
n_c	number of sites in the rate-determining step of the deactivation reaction
$n_s(t)$	number of sites active for cumene disproportionation at time-on-stream t
$n_{s,d}(t)$	number of sites not available for cumene disproportionation at time-on-stream t
$P(t)$	the probability that the site is accessible at time t
P_i	partial pressure of species i
Q_2	heat of adsorption of cumene, kcal/mol
$r_b'(t)$	rate of benzene formation due to cumene disproportionation as determined by the Voorhies correlation, g mol/min/g cat
$r_b''(t)$	rate of benzene formation due to cumene disproportionation as determined by the hyperbolic correlation, g mol/min/g cat
$S(t)$	the conditional probability that the site is not covered
t	time-on-stream, min

$x(t)$	conversion at time-on-stream t
$x_2(t)$	the fraction of cumene converted to benzene at time t
$x_2'(t)$	the fraction of cumene converted to benzene via cumene disproportionation at time t as determined by the Voorhies type correlation
$x_2''(t)$	the fraction of cumene converted to benzene via cumene disproportionation as determined by the hyperbolic correlation at time t
$x_3(t)$	the fraction of cumene converted to C_3's at time t
W	weight of catalyst

Greek symbols

α, β, γ, δ	constants employed in Eqs. (1), (2), (4), and (7).
$\phi(t)$	the probability of finding a site active at time t

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