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Design of Zeolite/Silica–Alumina Catalysts for Triangular Cracking Reactions

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Cracking catalysts, consisting of zeolite in an active matrix, may have properties that are superior to the sum of the properties of the component parts. This is due to the interplay between diffusion, reaction, and selectivity among the components. We consider the effect of distributing the zeolite in a nonuniform manner through the active matrix. The triangular reaction set, incorporating second-order reactions of gas–oil to gasoline and overcracked products with simultaneous first-order decomposition of gasoline to coke and overcracked products, is used. For the fresh composite catalyst, the (constrained) optimum distribution has the zeolite lying in a relatively narrow region near the external surface. A simple physical model is used to describe the changes in the catalyst properties with deactivation, say by coking. The location of the optimum band of zeolite is shown to change with the deactivation level of the catalyst. The selectivity of the optimally distributed catalyst at each level of deactivation is seen to go through a maximum as the level of deactivation is increased, i.e., the catalyst selectivity first increases with deactivation before decreasing.

INTRODUCTION

Catalysts used for the cracking of gas–oil fractions to gasoline-range fractions generally consist of a composite containing 5–20% zeolite (crystalline aluminosilicate) in a matrix which may be composed of amorphous silica–alumina. Noble metals and other constituents may be added for various reasons, but these are not of interest in the present case. Further details of these catalysts can be found in, e.g., Refs. (*1*, *2*). The zeolite component has a higher activity and better selectivity toward gasoline, compared with the amorphous matrix component, but the former also has a higher mass transfer resistance compared with the latter. The zeolite is more rapidly coked, but appears to be more resistant to the effects of deactivation by coking. The two components when combined form a unifunctional, multicomponent (UFMC) catalyst, with improved characteristics compared to the two components separately. The manner in which the zeolite is distributed through the silica–alumina matrix is expected to affect the properties and characteristics of the composite catalyst. In this paper, we examine the effect of distribution of zeolite on the activity and selectivity toward gasoline formation; in particular, we indicate that there is an optimum distribution of zeolite for maximum selectivity, and that the optimum distribution changes with the deactivation level of the catalyst. The question of a global optimum distribution is related to complex questions of economics and kinetics and will not be addressed here.

The problem of zeolite distribution has been addressed earlier for simple cases such as a maximum in activity or a maximum in selectivity for a simple series reaction set or a simple parallel reaction set. Dadyburjor (*3*) obtained a distribution for maximum activity for a change in size of the composite catalyst, as well as for increasing deactivation of the catalyst. A first-order reaction was considered, with reaction rate and diffusivity data consistent with those for the gas–oil fraction. For a

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fresh catalyst, the results indicate that the optimum distribution is one where the volume fraction of zeolite at the center of the pellet is twice the average value, and monotonically decreases with increasing distance from the center such that there is no zeolite at the external surface of the pellet. For a partially deactivated catalyst, the optimum distribution for maximum activity is different, however; qualitatively, it contains a maximum at some point between the center and the surface, and the location of that maximum can change with the level of deactivation.

Optimum distributions for maximum selectivity obviously depend upon the type of reaction set used. For a simple series reaction, with the formation and loss rates of the intermediate both taken to be of first order, Dadyburjor (*4*) showed that an optimum distribution would contain only the matrix component at the core, and a mixture of matrix and zeolite toward the outer surface of the pellet. As the catalyst deactivates, the maximum selectivity is obtained by moving the zeolite interface closer to the outside surface. The maximum selectivity at each level of deactivation of the catalyst decreases with the increase in deactivation level. For two first-order reactions in parallel, the maximum selectivity is obtained when pure zeolite is placed on the outer surface of the composite catalyst. In this case, the selectivity is seen to increase with increasing deactivation of the catalyst. However, this increase in selectivity is achieved at the expense of a catastrophic loss of activity so that, for this so-called "active surface" configuration, the overall yield (i.e., the total amount of desired product produced per unit loss of reactant, or activity × selectivity) decreases with increasing deactivation. For the parallel reaction, the maximum yield is obtained when the zeolite is distributed as a zeolite–matrix mixture toward the outside of the catalyst pellet. Increasing the level of deactivation changes the optimum distribution by requiring the zeolite–matrix mixture to be closer to the outside surface, quantitatively similar to the effect for maximum selectivity in the series reaction case. Also, the maximum value of the yield decreases with increasing deactivation level.

The simple first-order series and parallel reaction sets do not adequately represent the reactions occurring during the cracking process. The simplest realistic reaction set is the so-called "triangular" reaction network developed by Weekman and Nace (*5*). This reaction set is represented in Fig. 1. Here the (desired) gasoline product, component B, is related to the reactant gas–oil, component A, and to component C, consisting of the light fraction, coke, and coke precursors, by a combination of series and parallel networks. However, the triangular reaction network is more than a simple juxtaposition of the simple networks considered earlier. Because gas–oil is a mixture of compounds of widely different properties, Weekman and Nace proposed that the gas–oil reactions (a and c in Fig. 1) be second order in reactant. Because gasoline contains fewer components than gas–oil, they proposed that reaction b of Fig. 1 be first order in reactant. In the following sections, the triangular reaction network is used to obtain the optimum distribution of zeolite in the matrix; this is done for a fresh catalyst as well as for various partially deactivated catalysts.

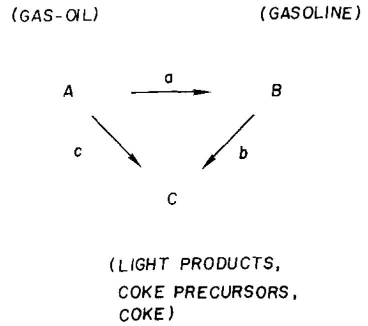

FIG. 1. Schematic of triangular reaction set of Weekman and Nace (*5*).

ANALYSIS

As for the cases of the series reaction and the parallel reaction, a three-zone flat plate is used to describe the catalyst pellet. See Fig. 2. Aris (*6*) has shown that the flat-plate geometry adequately represents any other arbitrary geometry, with perhaps a scaling factor included. The three zones consist of a matrix-only region, extending from the center to a fractional distance β toward the outside surface; a central zone consisting of a uniform mixture of zeolite and silica–alumina, extending from a fractional distance β to γ toward the surface; and a matrix-only region extending from a fractional distance γ to the outside surface of the pellet. It should be noted that the three-zone representation is a general formulation, and reduces to a number of special cases. These include the completely uniform distribution of zeolite in the matrix ($\beta = 0, \gamma = 1$), and the annulus of pure zeolite ($\gamma = \beta + \bar{\varepsilon}$, where $\bar{\varepsilon}$ is the average volume fraction of zeolite in the pellet). In each of three regions, reaction rates and mass transfer fluxes can be combined to yield a differential equation for the concentration of each of the three components. For instance, for component B in the central zone (r), we have

$$D_{\mathrm{Br}} d^2[B]_\mathrm{r}/dz^2 + k_{\mathrm{ar}}[A]_\mathrm{r}^2 - k_{\mathrm{br}}[B]_\mathrm{r} = 0 \quad (1)$$

The concentration profiles of A, B, and C can be obtained by solving the nine differential equations analogous to Eq. (1), together with boundary conditions and matching conditions. The boundary conditions are that there is no mass flux at the center, and that mass transfer outside the pellet is rapid so that the external surface concentration of the reactant is set equal to a fixed value ($[A]_L$) and the external surface concentrations of B and C are set equal to zero. The matching conditions are for concentrations and concentration gradients at the interfaces $z = \beta L$ and $z = \gamma L$. In the matrix-only zones, the values of the rate constants k and effective diffusivities D are those corresponding to silica–alumina alone. In the central zone, the values of the parameters are the weighted average of the zeolite and silica–alumina, e.g.,

$$D_{\mathrm{Br}} = \varepsilon D_{\mathrm{Bz}} + (1 - \varepsilon) D_{\mathrm{Bm}}, \quad (2)$$

with ε being the volume fraction of zeolite in the central ring, given by

$$\varepsilon = \bar{\varepsilon}/(\gamma - \beta). \quad (3)$$

Equation (2) is not strictly valid, particularly in the limiting case when the central zone consists only of zeolite particles, i.e., when $\varepsilon = 1$. However, it conveys at least the qualitative effects expected (*3, 4*). A relation similar to Eq. (2) may be written for the overall rate constants k_{ar}, etc., provided we assume that the zeolite particles in the central zone are small enough that the overall reaction rate in the zeolite is approximately equal to the intrinsic reaction rate in the zeolite. In our earlier work (*3, 4*), our calculations indicate that this assumption is reasonable.

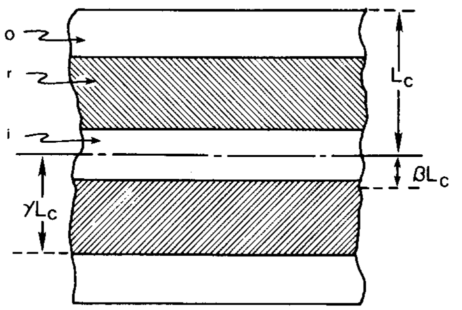

FIG. 2. Three-zone flat-plate formulation used to determine optimum distribution of zeolite. Inner and outer zones (i and o) contain matrix only. The central zone (r) extends from $z = \beta L$ to $z = \gamma L$, and contains a uniform distribution of zeolite in silica–alumina.

From the concentration profiles in the entire composite catalyst, the overall reaction rates can be computed. Then the overall selectivity of the catalyst is defined as the ratio of the net rate of formation of B to the net rate of loss of A:

$$S_\mathrm{B} = \{(D_\mathrm{B}/D_\mathrm{A})(d[B]/dz)/(d[A]/dz)\}_{z=L}. \quad (4)$$

The value of S_B will depend upon the value of β and the value of γ. Finding the optimum distribution of zeolite in the composite catalyst consists of finding the values of β and γ such that the value of S_B is a maximum. The values of S_B are obtained numerically as described in the following section.

NUMERICAL SOLUTION

The differential equations of Eq. (1) are two-point boundary value problems and are solved numerically using a shooting-type method. The relations for species A can be decoupled from the other species, enabling them to be solved independently. These second-order ordinary differential equations (ODEs) are converted to coupled pairs of first-order ODEs. An initial-value problem is created by guessing a value for $[A]$ at the center of the composite catalyst pellet ($z = 0$). The equations for species A in each section of the composite catalyst pellet are then solved sequentially, using the general purpose ODE solver LSODE (*7*). The guessed value of $[A]$ at the center is adjusted, using the modified Regula-Falsi method, until the value of $[A]$ at the external surface ($z = L$) as computed by LSODE converges to the known boundary condition $[A]_L$. When $[A]$ at $z = 0$ is determined, the relations for species B can be solved using a similar procedure, with the composition of species C then computed by the overall mass balance. This technique is repeated for all allowable values of γ for a given value of β, i.e., for γ between $(\beta + \varepsilon)$ and 1; then this is repeated for all allowable values of β, i.e., β between 0 and $(1 - \varepsilon)$. In this way, the optimum values of β and γ can be obtained for a given set of values for the reaction rate parameters, k, and the effective diffusivity parameters, D. The values given to these parameters for the fresh catalyst and for various partially deactivated catalysts are described in the next section.

SYSTEM PARAMETERS

The Base Case parameters given in Table 1 correspond to parameters expected for a fresh catalyst. The rate constants k for reactions a and b involving gas–oil as reactant are consistent with measured values of the intrinsic reaction rate over the zeolite component alone and the matrix component only, as reported in Ref. (*8*). The value of the concentration of A at the external surface,

$$[A]_L = 1.6 \times 10^{-5} \text{ mol/cm}^3,$$

required to estimate the rate constants from the rate data, is obtained by estimating the reactant to be pure *n*-hexadecane at 1 atm

TABLE 1

Parameter Values Used

Parameter	Units	Base case	Coking simulation case number				
			1	2	3	4	5
k_{az}	$\times 10^3$ cm^3/mol/s	10	8.2	6.4	4.6	2.8	1
k_{am}	$\times 10^3$ cm^3/mol/s	1	1	1	1	1	1
k_{bz}	$\times 10^2$ s^{-1}	8	6.6	5.2	3.8	2.4	1
k_{bm}	$\times 10^2$ s^{-1}	1	1	1	1	1	1
k_{cz}	$\times 10^2$ cm^3/mol/s	3	3	3	3	3	3
k_{cm}	$\times 10^2$ cm^3/mol/s	8	7	6	5	4	3
D_{Az}	$\times 10^{-5}$ cm^2/s	1	1	1	1	1	1
D_{Am}	$\times 10^{-5}$ cm^2/s	10^3	$10^{2.4}$	$10^{1.8}$	$10^{1.8}$	$10^{0.6}$	1
D_{Bz}	$\times 10^{-4}$ cm^2/s	1	1	1	1	1	1
D_{Bm}	$\times 10^{-4}$ cm^2/s	10^3	$10^{2.4}$	$10^{1.8}$	$10^{1.2}$	$10^{0.6}$	1
L	cm	0.002					
$\bar{\varepsilon}$		0.05					

and 500°C. The individual rate constants are assigned by noting that the zeolite is more selective than the matrix, so that

$$k_{az} \gg k_{cz}$$

and

$$k_{am} > k_{cm}.$$

Further, the zeolite cokes faster than the matrix, so that

$$k_{bz} > k_{bm}.$$

The values of the effective diffusivities for component A are consistent with the measured values of Ref. (*9*). Note that the value in the zeolite is several orders of magnitude smaller than that in the matrix. Values of the effective diffusivity for component B are estimated by noting that it must be able to diffuse much more readily than component A, due to the lower molecular weight of A. Values of the half-thickness, L, used are those found in commercial FCC catalysts. The commercial catalysts contain up to 20% zeolite.

For the deactivated catalyst, five different cases are considered in Table 1. In all of these cases, it is assumed that parameters that change as a result of deactivation do so uniformly across the catalyst pellet, i.e., that deactivation is uniform, rather than of the pore-mouth type. The quantitative model used for the deactivating catalyst here is analogous to that used in Refs. (*3*, *4*), and is as follows. For the same parameter in the two catalyst components, zeolite and matrix, the parameter which has the smaller magnitude is unchanged while that with the larger magnitude is decreased. This approach has been justified previously on physical grounds. Then, as can be seen in Table 1, k_{az}, k_{bz}, and k_{cm} decrease from the Base Case through Case 5, while k_{am}, k_{bm}, and k_{cz} are unchanged. Similarily, D_{Am} and D_{Bm} are decreased while D_{Az} and D_{Bz} are unchanged. For all parameters, Case 5 corresponds to the situation where the zeolite and matrix have identical values; this is unlikely to be achieved in practice, but is a convenient limiting case. Since the reaction rate constants in the fresh zeolite and matrix components are not too far apart in value, while the diffusion coefficients are several orders of magnitude smaller in the fresh zeolite compared with the matrix, the decrease in the rate constants is assumed to be linear from the Base Case to Case 5, and logarithmic for the values of the effective diffusivities.

For each of the sets of parameters in Table 1, the optimum location of the zeolite–matrix mixture (i.e., values of β^* and γ^*) are provided in the next section, as are the maximum values of the selectivity corresponding to each optimally designed catalyst.

RESULTS AND DISCUSSION

The effect of different distributions of zeolite for a fresh catalyst (Base Case) is shown in Fig. 3. The curve labeled "PURE ANNULUS" corresponds to the central zone consisting of pure zeolite, i.e., $\gamma = \beta + \bar{\varepsilon}$. Here the selectivity S_B decreases as β increases from a value of 0 to $(1 - \bar{\varepsilon})$, i.e., from an "active center" formulation, point C, to an "active surface" formulation, point S. The decreased selectivity as the zeolite band moves toward the outside surface is contrary to the results observed for the simple first-order parallel reaction set, and more closely resembles the results of the first-order series reaction set. For a given value of β, the inner limit of the central zone, the value of γ increases as matrix is introduced into the central region, and the effects of this are seen in the curve labeled "$\beta = 0$." With only a small amount of matrix introduced, the value of the selectivity rises sharply. Further incorporation of the matrix causes a slow but continuous increase in selectivity, so that for this value of β, the best location of γ is at the outer surface, corresponding to a uniform distri-

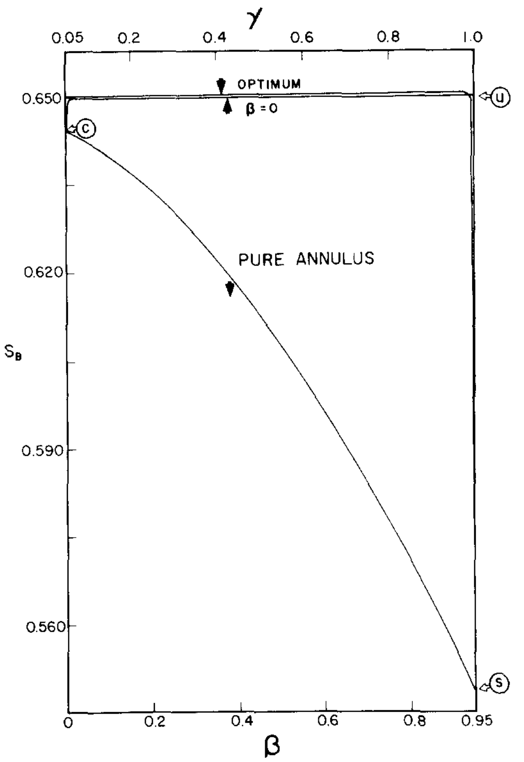

FIG. 3. Selectivity for various distributions of fresh catalyst using the triangular reaction set. Points C, S, and U refer to "active center" ($\beta = 0, \gamma = \bar{\varepsilon}$), "active surface" ($\beta = 1 - \bar{\varepsilon}, \gamma = 1$), and uniform ($\beta = 0, \gamma = 1$) distributions, respectively.

bution, point U. The addition of a small amount of matrix into the central region significantly increases the diffusivity in that region, while only marginally lowering the reaction rate constant. Further, the diffusivity effects are more pronounced for species A than species B, thereby favoring an increase in the rate of B. Curves similar to this one were generated for a number of values of β, ranging from 0 to $(1 - \bar{\varepsilon})$. In all cases, the maximum selectivity corresponds to $\gamma = 1.0$. The curve labeled "OPTIMUM" in Fig. 3 shows the values of the maximum selectivity as a function of β. The selectivity increases slightly as β increases, and exhibits a maximum at β approximately equal to 0.85, after which the selectivity falls off slowly. As β increases beyond 0.94, the selectivity falls off very rapidly, as the central region is once again converted to pure zeolite, and the selectivity reaches the value of the "active surface" distribution when $\beta = 0.95$.

For the fresh catalyst, therefore, the optimum distribution would appear to be a "dilute surface" distribution, composed of a core of matrix extending to 0.85 of the distance to the outside surface, surrounded by a zone containing zeolite and matrix in the ratio of 1 : 2. However, Fig. 3 suggests that this distribution may be exceedingly sensitive to variations in reaction rate constants and/or diffusivities, as would occur during coking.

Figure 4 shows the effect of zeolite distribution when the catalyst deactivates, with parameters changing from the Base Case (labeled "FRESH") to the limiting case when zeolite and matrix have the same low values (labeled "COKE 5"). The "FRESH" curve of Fig. 4 is identical to the "OPTIMUM" curve of Fig. 3. The six curves of Fig. 4 are qualitatively similar, showing a slight increase in selectivity as β increases up to a point, and then showing a dramatic drop in the selectivity for larger values of β. In every case, the maximum selectivity occurs at $\gamma = 1$ for all values of β, and this too is similar to the results of Fig. 3. As the coke level is increased, there is a monotonic decrease in the optimum location of β; there is also a less drastic drop in the selectivity as the value of β increases beyond its optimum location. But the most interesting effect observed on increasing the deactivation level of the catalyst is that the overall selectivities are actually seen to increase from the fresh case at least up to Case 2, after which the selectivity is seen to decrease. The shift in the location of the optimum β with increased coke levels indicates that increased amounts of matrix are needed in the central zone to counterbalance the decreasing diffusivities of the ma-

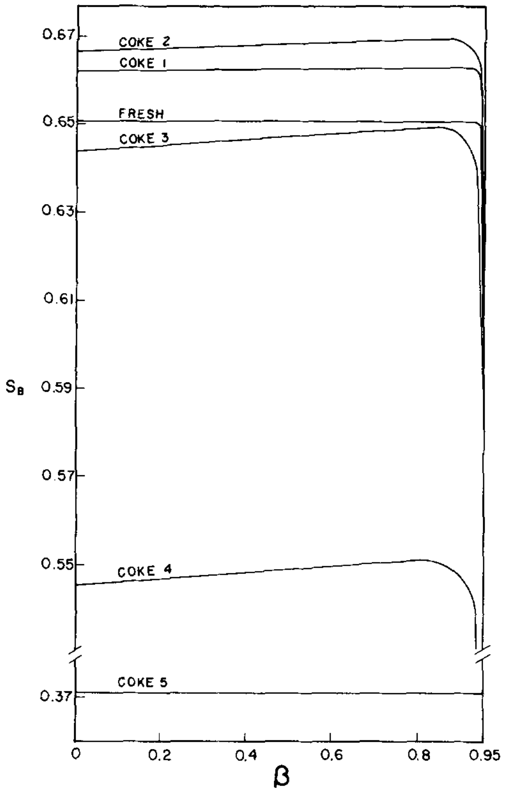

FIG. 4. Selectivity for different zeolite distributions for fresh and deactivating catalysts. Each point on each curve represents the maximum selectivity for the corresponding value of β when γ is a variable; the maximum of each curve represents the optimum location of β and γ. The curve labeled FRESH corresponds to the Base Case parameters of Table 1; COKE 1 through COKE 5 correspond to Cases 1 through 5 of Table 1.

trix. The "flattening" of the profiles occurs because the properties of the zeolite and matrix become less distinguishable—note the completely horizontal nature of the curve for Case 5. The initial increase in selectivity probably arises from the disproportionate lowering of the parameters. At low coke levels, the ratio k_{az}/k_{bz} decreases very slightly with coke level, and hence the zeolite selectivity is lowered only slightly. However, the matrix selectivity increases with a reduction in k_{cm}, and this increases the selectivity of the composite catalyst. As coking progresses, the sharper decline in zeolite selectivity probably offsets any increase from the matrix component.

Figure 5 summarizes the effect of coking on the maximum selectivity for various distributions of zeolite in the composite catalyst. The effect of coking on the selectivity is clearly shown. Also shown is the position of the inner interface of the zeolite–matrix mixture, and its variation to maintain maximum selectivity as the coke level increases.

SUMMARY AND CONCLUSIONS

The effects of distribution of a more active component in a less active, but not inert, component have been examined for the more realistic case of the triangular reaction set with higher-order reaction rates, used to model catalytic cracking. The optimum distribution to maximize the selectivity of the gasoline species (component B in Fig. 1) is a "dilute surface" distribution. While this distribution yields a larger selectivity than the uniform case, the actual improvements depend critically on the values used for the reaction rate constants and effective diffusivity. Deactivation of the catalyst is shown to increase the selectivity of the composite catalyst, possibly by decreasing the propensity of the catalyst to form unneeded products and coke precursors (component C in Fig. 1). The optimum location of the zeolite in the composite catalyst varies with the level of deactivation.

NOMENCLATURE

A, B, C	Reactants and products in triangular reaction set, Fig. 1; $[J]_y$, concentration of J (=A, B, C) in region y(=i, o, r).
$[A]_L$	Concentration of A at the external surface, $z = L$
a, b, c	Reactions in triangular set, Fig. 1
D_{Jy}	Effective diffusivity of J(=A, B, C) in region y(=i, o, r)
i	Inner matrix region of composite catalyst, Fig. 2

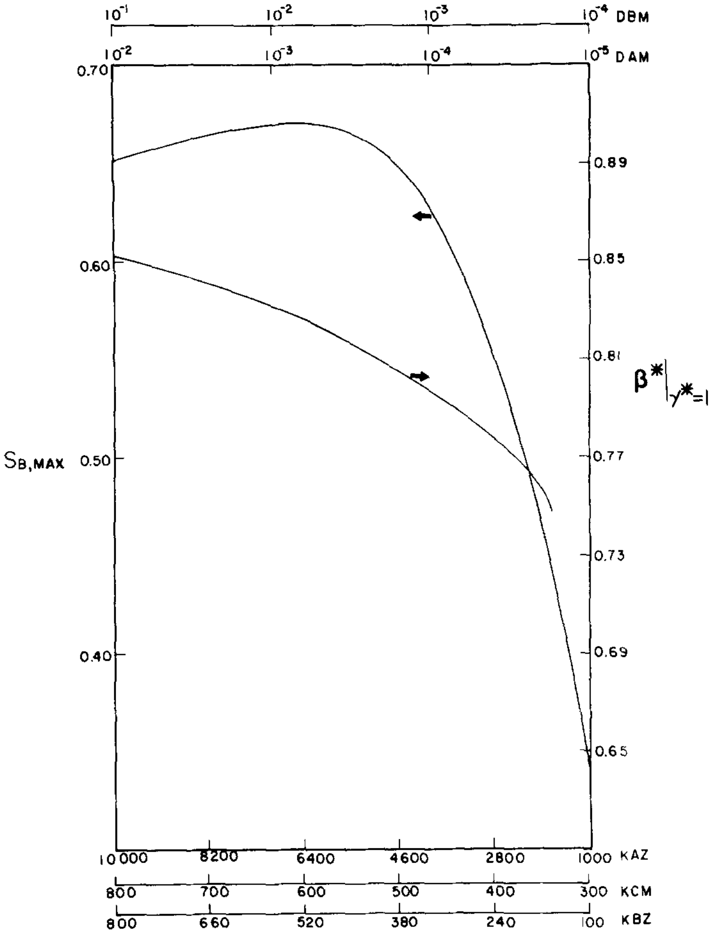

FIG. 5. Change in optimum distribution (β^*) and maximum selectivity ($S_{B,max}$) as the fresh catalyst is deactivated. In all cases, the optimum value of γ is $\gamma^* = 1$, the outer surface. Note the increase in the value of the maximum selectivity at intermediate values of the coke level.

k_{jy}	Rate constant for reaction j(=a, b, c) in region y(=i, o, r)
o	Outer matrix region of composite catalyst, Fig. 2
r	Central zone (zeolite/silica-alumina) of composite catalyst, Fig. 2
S_B	Selectivity of triangular reaction set for B, Eq. (4)
z	Distance coordinate, Fig. 2

GREEK

β	Location of inner interface of central zone, Fig. 2; β^*, location of β for maximum S_B, Fig. 5
γ	Location of outer interface of central zone, Fig. 2; γ^*, optimum location of γ for a given β
ε	Volume fraction of zeolite in central zone; $\bar{\varepsilon}$, overall volume fraction of zeolite in composite catalyst

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