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On the Development of a Catalyst Fouling Model

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A model of catalyst fouling is presented. It is based on a reaction network in which a hydrocarbon molecule is sequentially adsorbed onto a small group of active sites. Each intermediate species in this sequence is bonded to a different number of sites and treated as an independent fouling precursor. Thus, a series of parallel reactions are competing to foul the surface. The rate of each parallel step differs by an exponential factor equivalent to about 2 kcal/mol decrease in the fouling activation energy for each additional site involved in the rate determining step of fouling, and a simple power-model activity factor. The model provides an explanation of empirical fouling correlations and the apparent "variable reaction order" of fouling. The model is extended to include catalysts that are pretreated by a poisoning agent such as sulfur.

INTRODUCTION

A recently published correlation for catalyst fouling accounts for a remarkably wide range of data (*1*). The relation between activity and time is nonlinear on log–log coordinates. This suggests that a "variable reaction order" model is necessary to explain all the data if only uniform surfaces are considered.

Herington and Rideal (*2*) explained some peculiar variations in reaction rates for deactivating systems on uniform surfaces by accounting for reactions that occur on more than one site (i.e., multiplets of sites). In one case, they studied fouling that occurred on randomly located hexagonal multiplets on the (111) face of a transition metal catalyst. It was found that the population of these sextets approached zero when there were still approximately 40% of the sites unfouled. This calculation has been confirmed and it is observed that there should be an enormous drop in contribution to fouling via a sextet mechanism below an activity level of ~40%.

A simple sextet model does accurately represent fouling data above 40% activity for the dehydrogenation of methylcyclohexane (MCH) on reforming catalysts (*1*). However, this model appears to be a limiting case of the actual process. Based on the direction of the discrepancy between the data and the model at activities lower than 0.4, it is possible that fouling occurs on smaller multiplets as the sextets become exhausted. Furthermore, the limiting slope of the fouling correlation on the low activity extreme is indicative of fouling that occurs on very small multiplets, possibly doublets.

Catalyst fouling often occurs on a catalyst that has been pretreated to improve its stability. An example of interest herein is the Pt/Al_2O_3 reforming catalyst and its bimetallic successors. It is well known that an improvement in stability is observed after preexposure of such catalysts to a source of sulfur atoms (*3–5*). Thus, it is necessary to incorporate the effect of such pretreatments into this modelling effort.

This proposed transition in the operative fouling mechanism from the sextet to doublet fouling has been explored in detail and a model based upon this fouling process is presented herein. The model explains the entire range of variables covered in the empirical fouling correlation (*1*), extends the applicability of the power-model activity factor, and incorporates the effect of presulfiding as a stabilizing treatment.

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Multiplet Fouling Model

The basic idea of this proposal is that a number of rate processes are competing to deactivate the active surface. The kinetics of each process can be represented by a separable power-model activity factor. It is thought that the integer exponents used in each power-model factor are equal to the number of active sites involved in the rate-determining step (rds) of each process. All of these processes sum together to provide the rate expression governing the total rate-of-loss of active sites. The rate expression can be written as

$$dS_T/dt = -\sum_m k_m S_v[S_v/S_{T0}]^{(m-1)}. \quad (1)$$

The rate-of-loss of sites due to each independent process is proportional to the number of vacant sites times the fraction of adjacent vacant sites required in the rds raised to the $(m - 1)$ power. The rate constants k_m which incorporate the effects of gas composition and temperature are time invariant if the experiment are conducted in a reaction environment that is time invariant.

It is helpful to replace the number of vacant sites by a dimensionless fraction of the active sites that are vacant,

$$\nu \equiv \frac{S_v}{S_T} \equiv \frac{\text{number of vacant sites}}{\text{number of active sites}}. \quad (2)$$

It can be shown that a time-invariant reaction environment provides a constant vacant fraction ν as long as the site balance is linear.

It is also helpful to replace the total number of unfouled sites by a dimensionless fraction of the total sites that are active,

$$f \equiv \frac{S_T}{S_{T0}} \equiv \frac{\text{number of active sites}}{\text{number of active sites initially}}. \quad (3)$$

In order to nondimensionlize the time scale, it is helpful to introduce a dimensionless fouling time

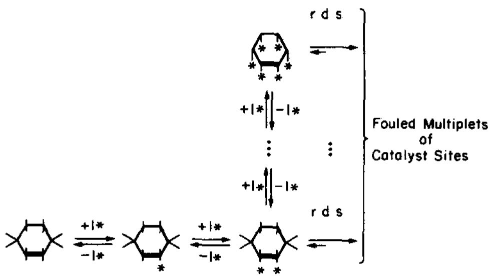

FIG. 1. Network of fouling reactions for multiplet fouling model.

$$\tau \equiv 5k_6\nu^6 t \equiv \text{dimensionless fouling time}. \quad (4)$$

This variable can be thought of as a deactivation reaction Damkohler number. The same arbitrary definition as used previously (*1*) is employed herein to allow a direct comparison of the results.

These definitions can be used to transform Eq. (1) into the dimensionless form

$$\frac{df}{d\tau} = -\frac{1}{5}\sum_m \left(\frac{k_m}{k_6}\right) \nu^{(m-6)} f^m. \quad (5)$$

The number of terms in the rate expression (i.e., the number of discrete values of m), the ratios (k_m/k_6), and the value of ν will depend on the mechanistic model of the deactivation system adopted. As an example of the application of this approach and in keeping with the goal of this study, it is appropriate to consider the case of MCH dehydrogenation over Pt/Al_2O_3.

The mechanistic model depicted in Fig. 1 helps illustrate the type of fouling reaction system that can explain the observed deactivation kinetics for the MCH system. The observation of central interest is the variable order of the separable activity function for the fouling reaction (i.e., the variation in slope of activity vs time). It is assumed that the rds of fouling reactions involve more than one active site, and the exact number of sites involved relates to the exponent (m) used in the power-model rate expression. Accordingly, a series of reactions each interacting with a different number of sites can explain the variable order implied by the observed correlation.

The reaction sequence in Fig. 1 is similar to the sextet model (*1*), except that each intermediate species is treated as an independent source of fouling. Assuming that all five reactions operate simultaneously, it is appropriate that Eq. (5) should be a summation from $m = 2$ to $m = 6$. Furthermore, it is reasonable to replace the rate constants (k_m) by the appropriate Arrhenius expressions

$$k_m = A_m \exp\{-E_m/RT\}. \qquad (6)$$

This model and these assumptions lead to the rate expression

$$\frac{df}{d\tau} = -\frac{1}{5}\sum_{m=2}^{6}\left(\frac{A_m}{A_6}\right)\nu^{(m-6)} \times \exp\left\{\frac{-(E_m - E_6)}{RT}\right\} f^m. \qquad (7)$$

At this point, there are obviously too many adjustable parameters for the result to have any practical significance. This can be remedied, of course, by making a couple of simplifying assumptions. First, differences in the preexponential and the coverage factors will be ignored. The mathematical statement of this is shown in Eq. (8). Second, it is assumed that the difference in activation energies ($E_m - E_6$) is proportional to minus the difference in the number of sites involved in the rds ($6 - m$), as indicated in Eq. (9). These assumptions will be discussed later.

Assume that for all values of m,

$$(A_m/A_6)\nu^{m-6} = 1, \qquad (8)$$

and

$$(E_m - E_6) = \lambda(6 - m), \qquad (9)$$

where $\lambda \equiv$ decrease in activation energy per additional site involved in rds of fouling.

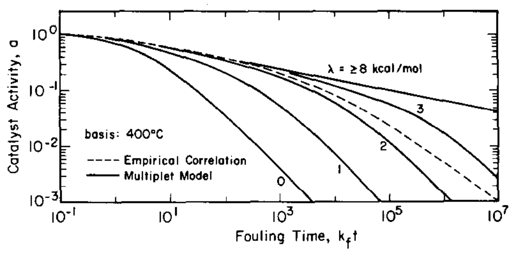

FIG. 2. Comparison of multiplet model with empirical fouling correlation for several values of λ.

These simplifications allow Eq. (7) to be written as

$$\frac{df}{d\tau} = -\frac{1}{5}\sum_{m=2}^{6} \omega_m f^m. \qquad (10)$$

where

$$\omega_m = \exp\{(m - 6)\lambda/RT\}. \qquad (11)$$

The exponential multiplet factor ω_m physically represents the ratio of the initial fouling rate of the mth process to that of the sextet process. The power model factor f^m is the separable activity factor for the fouling reactions.

In order to compare the model with the correlation, it is necessary to relate the fraction unfouled (f) to the observed catalyst activity (a). The activity is defined as the observed rate of the desired reaction normalized to the initial observed rate in the same reaction environment. Again, it is common to apply the separable power-model assumption to such reactions. The assumption is

$$a = f^n \qquad (12)$$

where n is referred to as the order of the main reaction, just as m was referred to as the order of the fouling reaction.

In this case, it is assumed that $n = 1$; that is to say, the activity equals the fraction of sites unfouled. The model (Eq. (10)) has been integrated numerically for several discrete values of λ at 400°C. A comparison of these integrations with the empirical fouling correlation (shown in Fig. 2) shows that this simple model works reasonably well for a λ of about 2 or 3 kcal/mol.

Prepoisoned Catalyst Fouling

The goal of the modeling up to this point has been to account for the fouling behavior of fresh unpoisoned catalysts. The initial activity has always been unity, corresponding to a catalyst in which all the sites are initially active. However, it is necessary to consider the case of a catalyst that is pretreated prior to fouling by a poisoning agent which eliminates some of the catalyst sites.

Catalyst fouling often occurs on a catalyst that has been pretreated to improve its stability. The example of interest is the presulfiding of a supported Pt/Al_2O_3 reforming catalyst and its bimetallic successors (*3–5*). It is observed that the multiplet model can be successfully applied to these cases.

The original multiplet model contains two parameters: the specific fouling rate (k_f)—which is a function of the fouling conditions such as temperature and gas phase concentrations of H_2 and the various hydrocarbon species, and the exponential multiplet parameter (λ)—which is a constant for the broad range of reaction systems considered. In applying the model to catalyst systems that have been pretreated by a poisoning agent such as sulfur, it is necessary to consider the initially activity of the catalyst as a third parameter that depends on the initial state of the catalyst. It is observed that typical sulfiding pretreatments affect the model in the following ways:

1. initial activity (a_0)—the model (Eq. (10)) must be integrated from the appropriate initial condition corresponding to the initial state of the catalyst;
2. specific fouling rate (k_f)—the specific rate may change thus altering the observed stability of the catalyst;
3. exponential multiplet parameter (λ)—this parameter is unaffected by sulfiding pretreatments and is essentially a universal constant.

As an example of how the model can be applied to prepoisoned catalyst system, it is helpful to show the fouling data for sulfided reforming catalysts in Fig. 3. The data were taken on a gradientless reactor described elsewhere (*6*). The main reaction is the dehydrogenation of methylcyclohexane. Both catalysts were irreversibly fouled with H_2S by exposing the catalyst to 5 molecules of H_2S per platinum atom. This was accomplished by introducing the necessary number of 3 cc aliquots of 1000 ppm H_2S into a flowing stream of hydrogen that passed over the catalyst at 500°C. The treatment provides a reproducible and apparently irreversibly sulfided catalyst as reported previously (*7*).

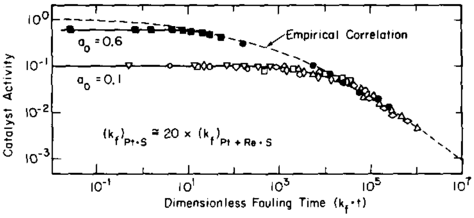

FIG. 3. Typical fouling data for sulfided reforming catalysts. Pt/Al_2O_3, shaded symbols; $Pt + Re/Al_2O_3$, open symbols.

All the activity data in Fig. 3 are normalized to the initial activity of an unsulfided Pt/alumina catalyst. The fouling data for unsulfided catalysts are well represented by the empirical correlation (*1*). However, in order to represent the fouling of sulfided catalyst systems, an additional parameter must be introduced. This additional parameter is equal to the normalized initial activity of the sulfided catalyst, a_0. Using this parameter as the initial condition for the numerical integration of Eq. (10), the curve segments (including the initial plateaus) shown in Fig. 3 are obtained.

There are several important observations that can be drawn from Fig. 3. First, the bimetallic catalyst is more sensitive to sulfur poisoning than the monometallic catalyst. This is shown by the sixfold lower initial activity of the former for the same pretreatment. Second, the sulfiding pretreatment affects the specific fouling rate of these catalysts differently. The specific fouling rate of either catalyst is typically lower than that of the fresh Pt/Al_2O_3 catalyst, accounting for the greater stability of the sulfided catalysts. Furthermore, k_f for the bimetallic is typically about 20 times less than that of the monometallic for the same pretreatment and the same fouling conditions (as indicated in Fig. 3), accounting for the even greater stability of the bimetallic catalyst. Finally, the value of λ is not affected by sulfiding for either catalyst.

Uniform Surface Calculations

It is quite common to use simple power-model expressions to relate rates of reactions occurring on a catalyst undergoing fouling. The exponents are usually described as the number of sites involved in the rate determining step (rds) of the reactions involved. This is stated algebraically in

$$[\mathcal{R}_1(t)/\mathcal{R}_1(0)]^{1/m_1} = [\mathcal{R}_2(t)/\mathcal{R}_2(0)]^{1/m_2}, \quad (13)$$

where $\mathcal{R}_i(t)$ is the rate of the ith reaction after deactivating for a length of time (t) in a constant reactor environment, and m_i is the number of sites involved in the rds of the ith reaction.

This type of expression implicitly assumes that the surface species (including the foulant) are completely mobile and that all vacant sites are equally accessible even after some deactivation has occurred. It is not obvious that these assumptions are reasonable for a catalyst undergoing severe deactivation. The intent of this section is to establish some justification for applying the simple power-model expressions that successfully account for the fouling data in the preceding sections.

A site matrix corresponding to the (111) face of metal particles ranging in size from ~20 to ~120 Å in diameter was used as a basis for all calculations. The calculations were performed on a Commodore PET personal computer and are directly analogous to the calculations of Herington and Rideal (2). The procedure is to "foul" a prescribed fraction of the surface sites and then evaluate the surface by counting the number of unique multiplets that are present at each level of deactivation.

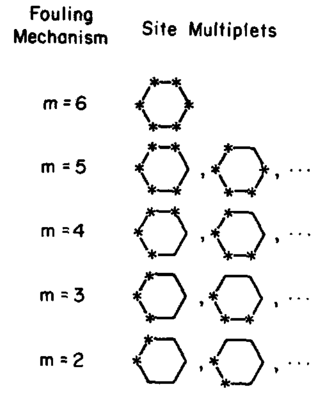

FIG. 4. Summary of various fouling mechanisms and the corresponding multiplets.

The multiplets corresponding to the various fouling mechanisms are summarized in Fig. 4. Fouling occurs by one mechanism at a time, beginning with $m = 6$, and continues until the surface is exhausted of that multiplet. The procedure is to select a site randomly in the matrix that is accessible to the operative fouling mechanism and foul the entire multiplet of sites. After exhausting the surface of a given multiplet, say $m = 5$, the random search is repeated at the next level, say $m = 4$. This process continues until the entire surface is void of any multiplets.

The surface is evaluated at various levels of "activity" by rastering across the site matrix and counting the number of each type of multiplet present. The notation P_m refers to the population of the mth multiplet normalized to unity for the fresh surface. Typical results of evaluation are shown in Fig. 5. The dashed lines show the relationship between P_m and P_1 (singlet vacancy). The solid lines show the relationship between P_m and P_{1A} (singlet vacancy with at least one adjacent vacancy). The dotted lines represent the power-model relationship between P_m and P_1 implied by Eq. (13), assuming that P_m is directly proportional to

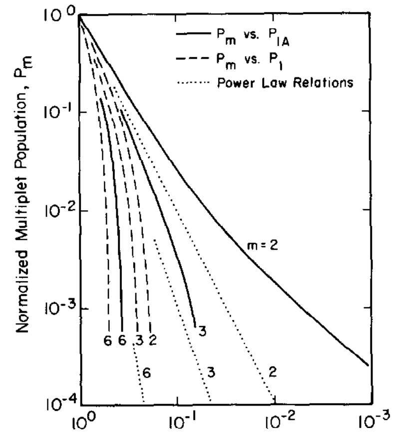

FIG. 5. Normalized multiple populations for a deactivating uniform (111) surface.

the rate of a reaction occurring on the *m*th multiplet.

The dashed lines in Fig. 5 demonstrate the same type of difficulty encountered by Herington and Rideal (*2*). The number of multiplets (P_m) falls off much too fast relative to the loss of singlets (P_I) for this calculational technique to account for the power-model relations (dotted lines). In an attempt to overcome this difficulty, the abscissa (P_I) is replaced by a new variable (P_{IA}). In this case (solid lines), the multiplets (P_m) are related to the number of unique singlets with at least one adjacent unfouled site. The idea is that while the rds may only require a single site, an adjacent site may be required for a relatively fast step or for sterric reasons. For example, associative adsorption of a hydrocarbon may be the rds requiring a single site. However, an adjacent site may be required for a relatively fast subsequent step. The result of this change is to get a little closer to the power-model relations, but it is not possible account for them completely using this type of calculation.

DISCUSSION

The MCH dehydrogenation reaction occurs principally on the metal function of the bifunctional reforming catalyst. It is a useful probe of the metallic function of this catalyst. The reaction is thought to occur uniformly over the metal surface on relatively small (one or two atom) active centers. With this picture, it is not too surprising that the fouling data for the MCH system can be explained on the basis of a simple separable power-model activity factor. However, it is quite surprising that this model also accounts for the wide range of additional reaction systems included in the empirical correlation, especially catalytic cracking (*8*). The unification of a large disparate data base implied by this observation is a major impetus of this work.

There are several ways of explaining the "variable reaction order" observed in the empirical fouling correlation. In order to avoid the temptation to consider nonseparable activity factors, it is necessary to consider a change in either the main or fouling reaction mechanism. Attention has been focused on the fouling reaction rather than the main reaction for several reasons. First, the shape of the empirical curve would imply that a large number of sites become involved in the rds of the main reaction at low activities, which is not anticipated. Second, the region of transition extends over several decades of activity indicating more than a single mechanistic change as might be expected for the main reaction. Finally, while the introduction of a simple exponential factor to account for the changing number of sites involved is justifiable in the case of fouling, this is not true for the main reaction.

It is worthwhile to note that the critical elements of the model which result in a favorable comparison with the correlation. Any model which is initially governed by a rate process such that ($n/m - 1$) equals $\frac{1}{5}$ and changes such that ($n/m - 1$) approaches 1 as the catalyst is severely fouled will curve-fit the correlation, provided that rate processes are weighted properly. Considering the MCH system, the range of $m = 6$ to $m = 2$ with an invariant $n = 1$ satisfies this requirement and allows a simple mechanistic interpretation.

It can be shown that for the range of $m = 12$ to $m = 4$ with an invariant $n = 2$, the correlation can be "curve-fit" even better. In fact, an extremely good curve-fit of the empirical correlation is provided by

$$\frac{df}{d\tau} = -10^{-1} \cdot f^{12} - 10^{-3} \cdot f^4, \quad (14)$$

$$a = f^2. \quad (15)$$

They are essentially represented by the dashed line in Figs. 2 and 3. But these equations do not lead to a mechanistic model which explains all the data as the model presented earlier does.

Justification for why the fouling activation energy for higher order multiplets is lower can be stated as follows. First, we note that fouling is a stoichiometric reaction as opposed to a catalytic reaction, since the catalyst is consumed in the process. It is also true that a surface reaction of a strongly adsorbed species must be rate determining, and at least some of the products do not leave the surface. In trying to apply the concept of a "volcano curve" to this reaction, there is no reason to expect a decrease in the reaction rate as the surface bonding interactions increase. Accordingly, a monotonic increase in fouling rate is expected as the number of sites involved increases. It is only speculation that this increase can be accounted for as an exponential factor effectively modifying the activation energy.

The empirically determined value of λ is apparently a universal constant, since the data in the original correlation come from a wide range of reaction systems. It is only a small fraction of the fouling activation energy and at this point there is no physical explanation for the magnitude of λ. Moreover, it is perplexing that a single value satisfactorily models all the data considering that small changes in this value have such an enormous effect on the results. It may be that small variations in λ contribute to the remaining difference in shape of the model versus the correlation observed in Fig. 2. But, it would be pointless to worry about small variations in λ as well as the poor fit between the model and the correlation at very low activity, since the lower portion of the correlation is based on only one data set (*8*) and the correlation is quite tentative in this region.

A key assumption in the development of this model is the dominating effect of the exponential factor. The mathematical statement of this assumption was shown in Eq. (8) and a few comments are appropriate. The left-hand side of Eq. (8) can be thought of as two separate factors: the ratio of pre-exponential factors A_m/A_6 and the ratio of initial multiplets due to differences in hydrocarbon coverage, $(\nu)^m/(\nu)^6$. The product of these two factors must be quite large in order for it to affect the results significantly, noting that for $\lambda = 2.3$, the initial rate of sextet fouling is about 1000 times faster than the initial rate of doublet fouling.

It is reasonable to immediately rule out the ratio of initial multiplets, since they can be expected to only account for a factor of about 3 or 4 at most (based on Herington–Rideal type of calculations). While it is not possible to rule out the possibility of large variations in the preexponential, the simplifying assumption (Eq. (8)) is made with the same spirit as the assumed invariance of λ (Eq. (9)); that is, to develop a model with a minimum of adjustable parameters.

It may be more satisfying to consider the ratio of initial fouling rates in this way: Ignore the variation of the initial multiplet populations but retain both the pre-exponential and exponential factors of k_m. In such a case, it may be possible to use a sort of "compensation effect," a little out of its normal context, to predict that the two factors should cancel each other. The exponential multiplet factor ω_m would then be a measure of the incompleteness of the compensation. The approach employed in this work is simpler and more useful.

It is important to draw a clear distinction between the exponential factor and the use of an Elovich type of equation. In this treatment, the adjustment of ΔE is attributed to the number of surface-adsorbate bonds on a homogeneous surface involved in a set of competing reactions. In an Elovich type of equation, the adjustment of ΔE would be attributed to the variation of heat of adsorption with coverage.

There is an interesting analogy between the dimensionless fouling correlation and a graphical technique for studying integral reactor conversion vs time data often referred to as Powell plots (*9*). In the case of fouling, a variable space velocity can be used to hold the main reaction at a stationary conversion level. However, the reactor behaves as a batch reactor in time as the catalyst is consumed, i.e., treat fouling as a stoichiometric reaction. In this context, the ordinate of the fouling correlation corresponds to the fraction of reactant (catalyst sites) remaining, and the abscissa corresponds to a dimensionless time.

This analogy is quite helpful toward understanding the fouling data. The dimensionless time may be more easily understood as a sort of deactivation Damkohler number (Da). For sufficiently small values of the Damkholer number, the activity of the catalyst will be essentially unaffected. This manifests itself as a horizontal plateau on the activity vs time coordinate in Figs. 2 and 3. In terms of the analogy, this corresponds to an integral reactor that is too small to obtain any measurable conversion.

It is interesting that one model with only two adjustable parameters (a_0, and k_f, where λ appears to be a universal constant) can account the fouling data of both the sulfided and unsulfided catalysts. It is very useful to note that one parameter can be principally associated with fouling (k_f), and the other parameter with the poisoning pretreatment (a_0). The potential of handling these effects separately is, of course, very attractive.

This model does support the contention that the greater stability of the bimetallic catalyst is to a large extent due to partitioning of the Pt particles (*10*). In the context of this model, the larger multiplets are eliminated on the sulfided catalysts at the expense of poisoning a fraction of the active sites. There will be a point where the greater stability does not sufficiently offset the loss in initial activity. Thus, an optimum in the benefit of sulfur poisoning is anticipated. It appears that the Pt–Re bimetallic holds a greater irreversible amount of sulfur poison and that this is closer to the optimum than a simple monometallic. However, this type of geometric (or ensemble) effect does not explain the cause of the greater sensitivity of the bimetallic catalyst towards sulfur or the improved stability (lower k_f) of the sulfided catalysts. Thus, an important aspect of the explanation is still unanswered.

It is correct that adatoms of sulfur on the (111) face of the platinum particle would effectively reduce the presence of large multiplets. However, there are other possible explanations for the stability effect of sulfur. One other interesting possibility stems from Somorjai's discussion of the surface reconstruction that can occur when the (111) face of platinum crystals are poisoned by sulfur (*11*). It is clear that reconstruction could also effectively reduce the population of large multiplets with the hexagonal geometry.

The results in Fig. 5, clearly do not justify or demonstrate the applicability of the simple power-model relations. However, the results are very important because they remedy a major weakness in the previous attempts to use this approach. It is quite clear from the dashed lines that relating the number of multiplets to the number of singlets on a deactivation surface, as done previously (*2*), is not useful. From such results one concludes that fouling would be governed by first-order kinetics ($m = 1$) for catalysts below about 10% activity since there is nothing left but isolated singlets. This is not observed and this problem can be partly remedied by redefining the abscissa. The new variable P_{1A} clearly improves the extent to which the uniform surface model can account for the power-model relations (esp. for P_6–P_3).

It is important to note that while the Herington–Rideal type of calculations are useful toward explaining the activity factor qualitively for each multiplet mechanism f^m, they provide no information about the ratio of the initial fouling rates. The introduction of a separate initial rate factor referred to as the "exponential multiplet factor" is necessary to explain the generalized fouling correlation.

Also noteworthy, the uniform surface calculations are, of course, unable to account for the absolute value of the specific fouling rate. Thus, some amount of experimentation is required to determine the values of k_f. However, with a minimum number of experiments, it is possible to obtain a very detailed account of the fouling process. This is accomplished by studying the effect of process variables on k_f, as previously demonstrated (*1*).

CONCLUSION

It is possible to explain the empirical fouling correlation by considering a series multiplet mechanism for fouling on an ideal Langmuir surface. This multiplet model provides a quantitative explanation of the role of presulfiding reforming catalysts.

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