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On a General Correlation for Catalyst Fouling

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A simple mechanism that models the fouling of a supported-metal-reforming catalyst accompanying the dehydrogenation of methylcyclohexane is presented and compared with published data for this system. The model of the fouling process is a Rideal–Eley type of mechanism. It correlates the data on catalytic reforming well in the region of high activity that is of greatest interest industrially. Published results from eight different fouling studies of reforming and catalytic cracking are used to obtain a more general fouling correlation between catalyst activity and reaction time and serves as an extension to the mechanistic model. The model and the empirical correlation provide a general framework for discussing some poorly understood questions including the definition and measurement of initial activity, the role of high pressure in commercial reforming, the low stability of cracking catalysts, and an explanation of the range of powers that are observed in power law rate expressions for catalyst fouling.

A great deal of research has been aimed at trying to obtain a basic understanding of the phenomena causing deactivation with the hope of developing more stable catalyst configurations (*1–3*). Deactivation phenomena are generally interpreted in terms of a separable deactivation function—a function that is a simple multiplier in front of the reaction rate expression (*4*). Although there are a few examples which do not fit this simple form such as nonideal surfaces (*5*) and nonlinear site balances (*6*), the separable deactivation function is almost exclusively used to describe catalyst deactivation.

In fundamental studies, the deactivation function is assumed to depend upon the kinetic variables of the system, such as temperature and concentration of the various species in the reaction mixture, for the same reasons that the rate of the main reaction depends upon these variables (*7, 8*). In applied studies, the deactivation function is assumed to be an empirical function of the time that the catalyst has been on steam (*9*), or the amount of a particular poison or foulant on the catalyst (*10*). Some authors have addressed the relationship between the fundamental and empirical approaches from a mathematical standpoint (*4, 9*). It has been demonstrated that the commonly used empirical correlations between activity and catalyst age (i.e., linear, exponential, and hyperbolic) can be derived from power law rate expressions for the main and fouling reactions with reasonable assumptions about the powers used for the activity factor (*4*).

In the cases cited here and in many others concerning the application of power law rate expressions to surface reactions, it is commonly assumed that the number of sites required to perform a given reaction and the exponent used on the activity factor in the rate expression are equal. The numerical calculations performed by Herrington and Rideal (*11*) cause considerable concern over the applicability of simple power law rate expressions for demanding surface reactions such as fouling. In fact, there is a definite need to verify the commonly made assumptions concerning the number of sites involved and the applicability of power law rate expressions in these reactions.

A model reaction system that has been studied under well-defined conditions with respect to fouling is the dehydrogenation of

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methylcyclohexane (MCH) over a supported-platinum-reforming catalyst Jossens and Petersen have reported the results of a detailed process variable study for this model reaction system (*12*) Their study was conducted using a variable space velocity reactor which allowed the acquisition of fouling data under reaction conditions that were held constant in both space and time (*13*) This constant environment study provides an unprecedented opportunity to develop and test the kinetics of a model fouling reaction

The original goal of the present work was to derive a simple rate expression for the fouling reaction from a reasonable reaction mechanism for the MCH system and compare the theoretical results with the data of Jossens and Petersen The comparison revealed some interesting problems such as the ability to define and measure the initial activity of a catalyst and the variation of reaction order with respect to activity These problems lead to the observation of a fouling correlation that is common to both reforming and cracking The purpose of this paper is to present the proposed mechanism and the empirical fouling correlation

FOULING REACTION MODEL

The deactivation process in catalytic reforming consists of progressive dehydrogenation, isomerization, and polymerization of hydrocarbon molecules on the active metal catalyst surface sites (*14*), with paraffinic molecules and aromatic molecules both contributing to the loss of catalytic activity A reasonable fouling mechanism might therefore begin with a paraffinic molecule being sequentially adsorbed onto a group of active metal sites losing a large number of hydrogen atoms in a series of reversible dissociative adsorption steps This multiply bound surface carbon skeleton reacts with gas-phase aromatic molecules in a Rideal–Eley manner that initiates a site-consuming polymerization process For MCH dehydrogenation, it will be assumed that MCH is bound to a sextet of sites on the surface losing all 11 hydrogen atoms in the ring, and that toluene is the only source of aromatic molecules This fouling mechanism is depicted as an integral part of the main reaction mechanism in Fig 1

The main reaction mechanism shown in

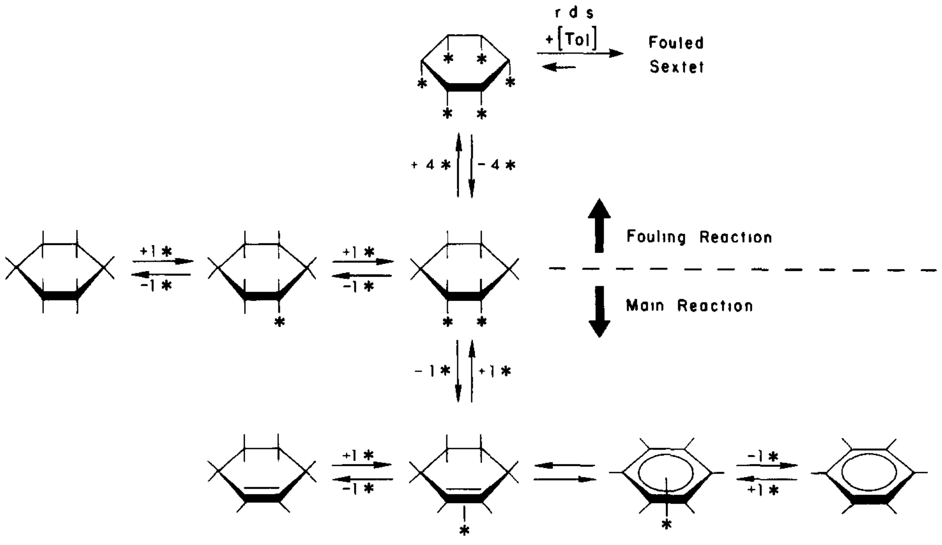

FIG 1 Six-site fouling mechanism as a parallel pathway to the main reaction mechanism (* represents active metal sites)

Fig 1 is similar to other presentations of cyclohexane dehydrogenation (*15*) It is assumed that the surface reaction step between the multiply bound carbon skeleton and toluene is the rate-determining step (r d s) for the fouling process By applying the equilibrium approximation for all the preceding steps, the rate expression for the loss of active sites shown in Eq (1) can be obtained (see Appendix)

$$\frac{dS_t}{dt} = -6k_f K_6 S_v^6 \frac{[\mathrm{MCH}][\mathrm{TOL}]}{[\mathrm{H_2}]^{11/2}} \qquad (1)$$

A relationship between the number of vacant sites (S_v) and the number of unfouled sites (S_t) must be introduced in order to integrate Eq (1) Product inhibition of the main reaction has been observed at the conditions of interest, and the inhibition is proportional to toluene to $-\frac{1}{3}$ power (*12*) This can be interpreted as a surface heavily covered with adsorbed toluene where the coverage is proportional to S_v and toluene to $\frac{1}{3}$ power as shown in Eq (2) This empirical result from the main reaction kinetics permits the integration of the rate expression (Eq (1)) The result is a hyperbolic activity decay function (Eqs (3) and (4)), assuming that activity is proportional to the number of unfouled sites The initial condition used in the integration is $S_t = 1$ Note that this integration now limits the application of Eqs (3) and (4) to deactivation in a reactor environment that is held constant throughout the deactivation process

$$S_t = K_3 S_v [\mathrm{TOL}]^{1/3} \qquad (2)$$

$$a = (1 + kt)^{-1/5} \qquad (3)$$

$$k = \frac{30 k_f K_6 [\mathrm{MCH}]}{K_3^6 [\mathrm{TOL}][\mathrm{H_2}]^{11/2}} \qquad (4)$$

It is now useful to compare Eqs (3) and (4) with the results of Jossens and Petersen The fouling data can be plotted as activity to the −5 power versus time in order to obtain numerical values of the parameter, *k* However, because of the large negative value of the exponent, such plots are very sensitive to experimental error The actual values of *k* are best determined by looking at log–log plots of activity versus time from which the appropriate values for *k* are easily obtained

The values for *k* and the fouling data at various process conditions are shown in Fig 2 where the appropriate *k* values have

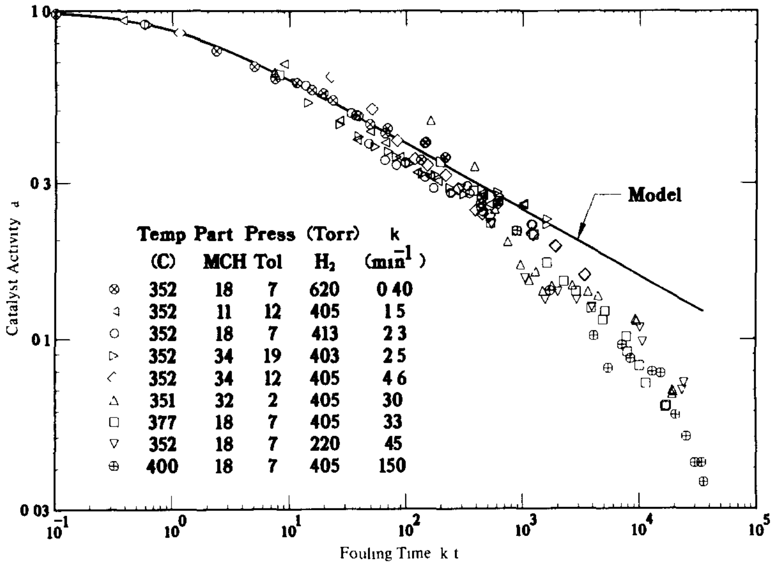

FIG 2 Six-site fouling model Fouling data for the dehydrogenation of methylcyclohexane over a $\mathrm{Pt/Al_2O_3}$ reforming catalyst (Ref (*12*))

been used to nondimensionalize the time coordinate The curve shown in Fig 2 represents the model (Eq 3) The dependence of k on the various process variables is shown in Figs 3–6, the solid lines in Figs 3, 4, and 5 indicate the effect predicted by the model (Eq (4)), and in Fig 6 the line indicates an apparent activation energy of 74 kcal/mol for the fouling reaction

It must be pointed out that the data shown in Fig 2 have been corrected to account for fouling that occurs prior to the first activity measurement The initial activity is determined by assuming that the steady state solution (Eqs (3) and (4)) is applicable during the initial reactor transient prior to any activity measurements That is, the fouling reaction is zero order with respect to the gas-phase concentrations during the transient, and the magnitude of the k defined in Eq (4) is determined by the steady-state conditions This has already been shown to be a very good approximation for determining the activity loss during the reactor transient (*6*)

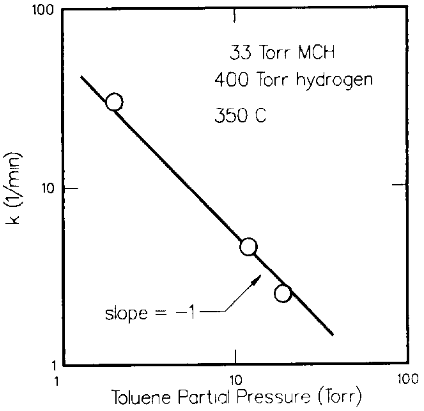

FIG 4 Toluene dependence Effect of toluene partial pressure on specific fouling rate for MCH dehydrogenation over Pt/Al_2O_3 (line represents the theoretical slope in Eq (4))

VARIABLE REACTION ORDER

The curvature of the data away from the model that is so apparent in Fig 2 lead to the investigation of a variable order power law model A variable order power law activity decay correlation is partly consistent with the phenomenological hyperbolic decay model discussed in the literature (*4*, *9*) The form of this model is reviewed in Eq (5), and the following terminology is used a is the deactivation function, t is reaction time, m is the fouling reaction order, n is the main reaction order, and k is a specific fouling reaction rate defined as the rate of fouling divided by the fraction of active sites remaining raised to the mth power This hyperbolic expression collapses into the simpler power law expression when kt

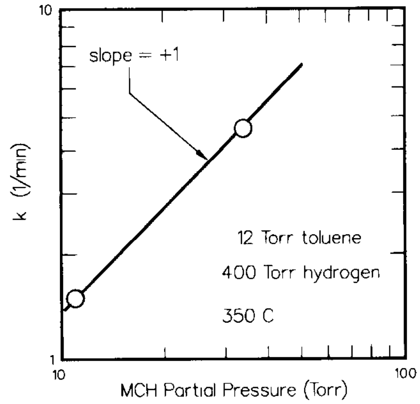

FIG 3 MCH dependence Effect of methylcyclohexane partial pressure on specific fouling rate for MCH dehydrogenation over Pt/Al_2O_3 (line represents the theoretical slope in Eq (4))

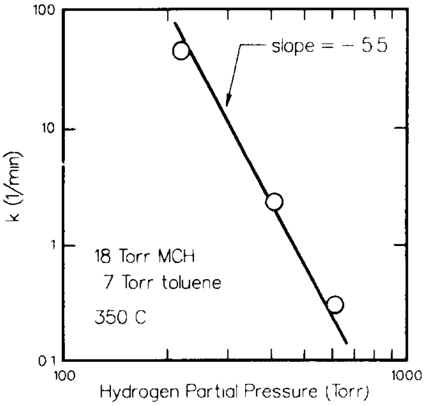

FIG 5 Hydrogen dependence Effect of hydrogen partial pressure on specific fouling rate for MCH dehydrogenation over Pt/Al_2O_3 (line represents the theoretical slope in Eq (4))

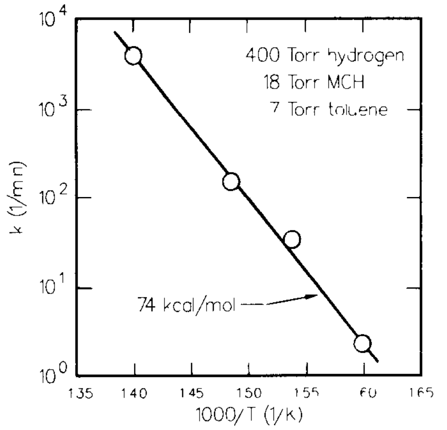

FIG 6 Temperature dependence Effect of temperature on specific fouling rate for MCH dehydrogenation over Pt/Al_2O_3 (line represents the apparent activation energy for fouling)

is much greater than unity It is important to emphasize that the power law decay function is a special case of the hyperbolic function, since the former is undefined at $t = 0$ Moreover, the continually changing slope observed in Fig 2 implies that the order of either the main reaction, the fouling reaction, or both, vary as the activity changes due to fouling

$$a = (1 + kt)^{n/(1-m)} \tag{5}$$

The observed "variable reaction order" is even more pronounced if Fig 2 is extended to incorporate a broader spectrum of fouling data Fig 7 shows the data from a wide range of fouling studies where the reaction orders cover a range of values such that the quantity $n/(m - 1)$ varies from $-0\ 2$ to $-0\ 5$ The sources of the fouling data in Fig 7 are indicated by the reference numbers in the symbol key The placement of the individual data sets onto Fig 7, and therefore the magnitude of k, is chosen to provide a smooth continuous curve between the high reforming activity of Jossens and Petersen (*12*), and the low cracking activity of Blanding (*16*) The location of these two extremes is not arbitrary since both studies provide a reasonable estimate of the initial catalyst activity

DISCUSSION

The data used to test the fouling model were obtained from a well-characterized reaction system in which the particle effectiveness factor was quite close to unity (*13*) This is important since it has been suggested that fouling kinetics can be masked by mass transfer limitations (*17*) in

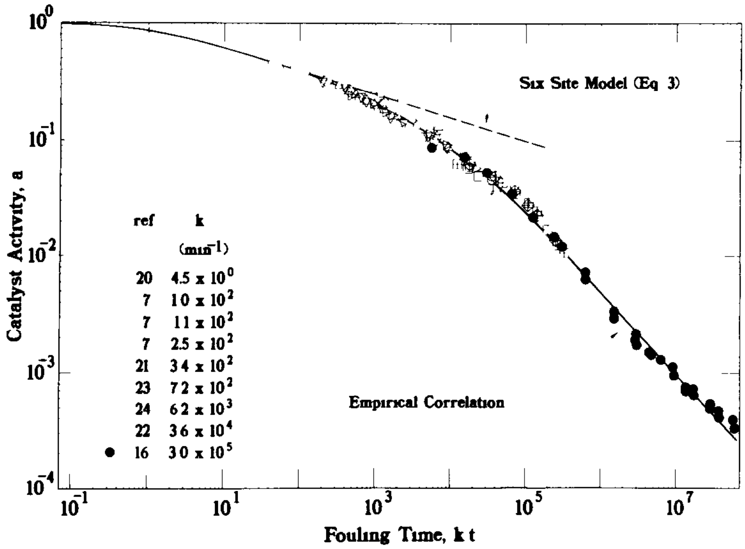

FIG 7 Dimensionless fouling correlation Variable reaction order fouling correlation for a wide range of specific fouling rates

a manner very analogous to the well-established behavior for main reaction kinetics (*18*) It is interesting to note that Blanding (*16*) observed $(n/m - 1) = 0\ 5$ on a reaction system that was similar, except for catalyst particle size, to that for which Voorhies (*19*) observed $(n/m - 1) = 0\ 2$ This change in reaction orders may be due to the effect of mass transfer on the fouling reaction order and it is directionally consistent with the theoretical work on parallel fouling (*17*)

The observation of decreasing activation energy with increasing temperature for systems that are not limited by mass transfer or chemical equilibrium is often attributed to fouling that occurs prior to the initial activity measurement Jossens and Petersen observed such an effect (*12*) One of the benefits this model provides is a means of estimating the fouling that has occurred prior to the first activity measurement (i e , extrapolate to $t = 0$)

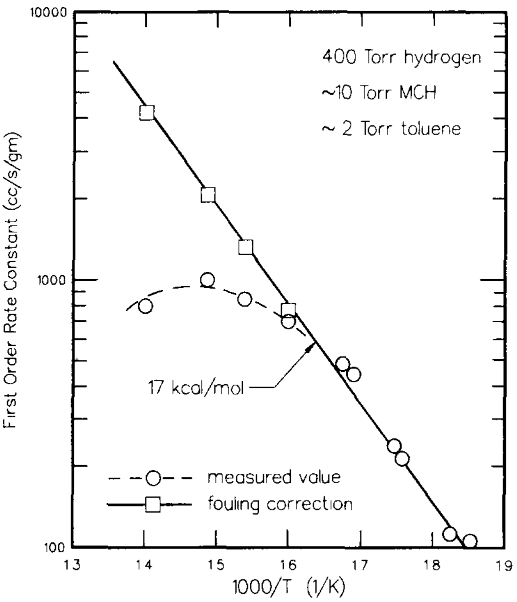

FIG 8 Main reaction Arrhenius plot Effect of fouling on main reaction Arrhenius plot for MCH dehydrogenation over Pt/Al_2O_3

In Fig 8, the initial activity data are shown along with the estimated amount of fouling that has occurred prior to the initial measurement on an Arrhenius plot This result supports the contention that the activation energy is indeed constant and the usual rationalization of this phenomenon is reinforced by the model

Another phenomenon that is supported by the model is the inhibition of fouling by aromatic products It was first shown by Heinemann (*25*) that adding small amounts of benzene reduced fouling that occurs during the isomerization of methylcyclopentane over a chromia–alumina catalyst A similar effect is observed here, as demonstrated by the dependence of k on toluene concentration (Fig 4) The explanation of this effect is competitive adsorption and is consistent with the empirically observed product inhibition of the main reaction (*12*)

The model is especially interesting in that it provides a functional explanation of the high pressures used in commercial reformers It is often noted that the stability of a reforming catalyst is a function of both the hydrogen to hydrocarbon ratio and the absolute value of their concentrations It is apparent from the concentration dependence shown in Figs 3–5, that k has about a -5-order dependence on hydrogen and a much less significant dependence on the hydrocarbon concentrations If the model is applicable at the higher pressures used in a commercial reformer, k is the order of inverse years (due to the high hydrogen pressure) thereby accounting for the stability of the catalysts in these reactors The prospect of extrapolating high severity results to predict those of low severity is of course the major impetus for this study and studies of high severity fouling in general

The remarkably high activation energy for fouling of 74 kcal/mol obtained in Fig 6 is worthy of some discussion We note the bond dissociation energies for some pertinent bonds in benzene and toluene in Table 1 It is well established that free radicals play a major role in the fouling of catalytic cracking catalysts So we speculate that radicals formed by rupturing one of the bonds listed in Table 1 are involved in the

TABLE 1

Selected Bond Dissociation Energies (Ref (*26*))

Bond	$D(R{-}H)^a$ (kcal/mol)
$C_6H_5{-}H$	103
$C_6H_5{-}CH_3$	91
$C_6H_5CH_2{-}H$	77

[a] The bond dissociation energy is defined as the heat of reaction for the formation of the two separate gas-phase radicals from the gas-phase molecule (e g , $C_6H_5{-}H \rightarrow C_6H_5 + H$)

$$D(C_6H_5{-}H) = \Delta H^\circ_F(C_6H_5) + \Delta H^\circ_F(H) - \Delta H^\circ_F(C_6H_5{-}H)$$

r d s of fouling for this model reforming system Thus, the aromatic molecule acts as a source of these gas-phase radicals Such a role can explain the first-order dependence on toluene shown in Eq (1) and the order of magnitude of the activation energy shown in Fig 6

The success of this model at high catalyst activity is certainly very interesting and it provides some useful perspectives on the overall fouling process However, it is undoubtedly a limiting case as shown by Fig 7 In the case of commercial reformers, this limited region may be more than sufficient to describe the fouling process, since reforming catalysts are not taken to very low levels of activity Catalytic cracking catalysts, on the other hand, are known to deactivate so rapidly that within a few seconds on stream the catalyst has lost more than an order or magnitude of activity (*16*)

The data in Fig 7 come from a variety of reaction systems hydrogenation of isobutene over nickel on kieselguhr (*20*), dehydrogenation of MCH over molybdenum on alumina (*7*), isomerization of methylcyclopentane over platinum on alumina (*21*), hydrogenolysis of cyclopropane over platinum on alumina (*23*), dehydrogenation of butene over chromia–alumina (*24*), cracking of hexadecane over zeolite (*22*), and cracking of petroleum gas oil over a synthetic cracking catalyst (*16*) Unfortunately, these studies do not provide the type of process variable study that is available for the MCH system, and therefore it is not possible to develop a model that can explain the all the data

The curvature (variable reaction order) observed in Fig 7 makes it impossible to develop a successful fouling model based on any single power law rate expression for the fouling reaction So for catalysts that are fouled over a large range of activity, it can be said that there are a number of processes that are competing to foul the catalyst, and as the activity changes so does the dominant mechanism for fouling Within any small range of activity, i e , less than a decade change, the slope of the empirical curve in Fig 7 does not change significantly As a consequence, fouling models based on a reasonable fouling reaction order appear valid The dominant fouling mechanism may not change within these limited ranges Accordingly, some simple and useful correlations would be expected between *k* and the pertinent process variables

The trial and error procedure used to construct Fig 7 is based on the property of logarithmic coordinates that the shape of a curve does not change when multiplied by a constant Thus, the orientation of any given set of fouling data is fixed, but the magnitude of *k* is chosen to provide continuity between the various fouling studies There were only two references that provided an initial activity These are Jossens and Petersen (*12*) and Blanding (*16*) It was the remarkable continuity between these two sets of fouling data taken on entirely different reaction systems that encouraged the development of this empirical correlation The asymptotic approach to an initial activity seen in Fig 7 is not obvious from any of the low activity experiments, and kept conscientious workers from developing any such log–log correlation

It must be mentioned that all of the data in Fig 7 are susceptible to experimental error, and that the exact location of the empirical curve is not well established In fact, the location of the empirical curve is sensitive to the value of the initial activity, and since only two references provided such measurements it must be concluded that the location of this curve is somewhat tentative Nonetheless, Fig 7 correlates all the fouling data for a large group of reaction systems

SUMMARY

The proposed mechanism for catalyst fouling models the MCH dehydrogenation reaction system very well at high levels of catalyst activity This mechanism appears to be a "limiting case" of an empirical fouling correlation that spans more than 3 orders of magnitude in catalytic activity This fouling correlation has several distinct attributes a definition of initial activity that has a well-defined upper limit asymptotically approached as fouling time approaches zero, a dimensionless coordinate system that greatly increases the utility of the correlation for design and evaluation purposes, and a single parameter that is a quantitative measure of catalyst stability Moreover, the correlation appears to unify otherwise unrelated collections of data and provides a common basis for evaluating catalyst stability

APPENDIX

The fouling reaction path proposed in Fig 1 can be summarized by an equilibrium step (Eq (A-1)) followed by a slow step (Eq (A-2)) The rate of loss of sites is given by the forward rate of the slow step (Eq (A-3)) The concentration {MCH*$_6$} can be written in terms of the equilibrium expression (Eq (A-4)) These equations lead directly to the expression introduced in the body of the paper (Eq (1))

$$\mathrm{MCH(g)} + 6^* \overset{K_6}{\rightleftharpoons} \mathrm{MCH}^*_6 + 11/2\,\mathrm{H_2(g)} \qquad \text{(A-1)}$$

$$\mathrm{MCH}^*_6 + \mathrm{TOL(g)} \xrightarrow{k_f} \text{Fouled Sextet} \qquad \text{(A-2)}$$

$$\frac{dS_t}{dt} = -6k_f\{\mathrm{MCH}^*_6\}[\mathrm{TOL}] \qquad \text{(A-3)}$$

$$\{\mathrm{MCH}^*_6\} = K_6\,\frac{[\mathrm{MCH}]\,S_v^{\,6}}{[\mathrm{H_2}]^{11/2}} \qquad \text{(A-4)}$$

LIST OF SYMBOLS

a	activity function for main reaction
D	bond dissociation energy
ΔH^0_f	heat of formation
k	fouling parameter in hyperbolic decay function
k_f	rate constant for r d s of fouling reaction
K_3	adsorption equilibrium constant for toluene
K_6	adsorption equilibrium constant for fouling precursor
m	fouling reaction order
n	main reaction order
S_t	number of unfouled sites
S_v	number of vacant sites
[ ]	used to indicate gas-phase concentrations
{ }	used to indicate surface species concentrations

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