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Research Note

Development of a Power-Law Expression for Catalyst Deactivation in Liquid-Phase Isobutene Alkylation

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The differential form of the decay law for a solid acid catalyst in liquid-phase alkylation of isobutane with butenes was investigated. A pseudo-first order expression for the intrinsic rate of the main reaction and a pseudo-second order one for the poisoning reaction were assumed. The role of intraparticle diffusion on the apparent deactivation behavior was studied through the Shell Progressive Model (SPM), as the overall reaction is severely diffusion limited. The decay rate law was found to be fourth order in pellet activity and second order in external butene concentration. The effect of pore-mouth plugging was also studied. It was shown that this phenomenon causes an increased deviation from the SPM predictions and lowers the average order of deactivation. An empirical order of deactivation of 2.3 was obtained for zeolites. This value, being considerably lower than four, implies appreciable pore-mouth plugging effects in the case of zeolite catalyzed alkylation.

INTRODUCTION

Alkylation is a refinery process for the production of gasoline-range isoparaffins from C_4 refinery cuts. Alkylates are ideal gasoline-blending stocks, due to their clean-burning characteristics. Because of several drawbacks associated with current liquid acid catalyzed processes [1], there is a great interest in the development of alternative solid-catalyzed processes. The major problem for the commercialization of solid acid catalyzed processes is their too rapid catalyst deactivation. Therefore, catalyst stability is a major issue towards the success of such processes.

In this work, the suitability of a power law expression for catalyst deactivation, proposed by Levenspiel [2], is investigated for the liquid-phase alkylation. The deactivation phenomenon is treated by the Shell Progressive Model (SPM) and the role of pore-mouth plugging on the overall deactivation behavior is considered. The detailed derivation of the deactivation rate law is discussed and the results are tested against the numerical solution of the governing equations, as well as the available experimental data.

THEORETICAL BACKGROUND

Basic Chemistry and Mechanism

Isobutane alkylation involves the reaction of isobutane with light olefins (mainly butenes) to produce heavier, highly branched isoparaffins (alkylates). The reaction may be represented as follows:

$$\mathrm{I} + \mathrm{O} \rightarrow \mathrm{A}, \tag{1}$$

where I stands for isobutane and O and A stand for olefin and alkylate, respectively. In the presence of acidic catalysts, the reaction proceeds through a chain mechanism via carbocation intermediates. Numerous secondary reactions occur simultaneously along with the desired Reaction 1. The main competing (i.e. undesired) reaction is olefin oligomerization, for example:

$$\mathrm{O} + \mathrm{O} \rightarrow \mathrm{D}, \tag{2}$$

where D represents a dimer. Other reactions include isobutane self-alkylation, disproportionation and cracking reactions. The detailed chemistry and mechanism have been discussed elsewhere [3,4].

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Like other hydrocarbon reactions in the presence of acidic catalysts, the presence of olefins in the feed and/or products (e.g. through Reaction 2), causes deposition of carbonaceous material or "coke" on the catalyst surface which eventually leads to its deactivation. Here, the oligomerization reaction (i.e. Reaction 2) is the main route for production of heavier olefins, which produce nondesorbable cations upon adsorption on active sites. Both individual site poisoning [5,6] and pore plugging [7] have been proposed as possible causes of deactivation.

The desired reaction is "first order" in olefin concentration, while the undesired reaction, is "second order" in olefin concentration. Therefore, a high I/O ratio in the reaction zone enhances both the alkylate selectivity and the catalyst lifetime. This may be achieved by using a high I/O ratio in the feed, working in high olefin conversions or using a back-mixed mode of operation [8].

Kinetic Formulation

It has been shown that the liquid-phase alkylation of isobutene is strongly intraparticle diffusion limited [9]. Therefore, any attempt to formulate catalyst deactivation should consider the effect of diffusion, in addition to the intrinsic poisoning kinetics. When the concentration of isobutane is in large excess to that of butene, as is the case in practice, the isobutane concentration may be considered constant during the course of reaction. Consequently, the reaction and poisoning rates become only functions of butene concentration. Under such circumstances, the following expressions for the intrinsic rates of main and poisoning reactions, respectively, might be proposed:

$$-r_B = k_A \alpha C_B, \tag{3}$$

$$-\frac{d\alpha}{dt} = k_P \alpha C_B^2, \tag{4}$$

where $-r_B$ is the rate of butene consumption per catalyst volume and k_A and k_P are the pseudo-rate constants of alkylation and poisoning reactions, respectively. Furthermore, α is the catalyst point activity and C_B is the butene local concentration. These intrinsic kinetics are consistent with the mechanistic models of Simpson et al. [9] and de Jong et al. [10].

The prevailing strong pore diffusion resistance affects both the rates of the main and poisoning reactions. For a parallel deactivation mechanism in the presence of strong pore diffusion limitation, initially most of the fouling occurs in the outer regions of the catalyst pellet where the concentration of olefinic reactant (i.e. poison precursor) is highest. As the olefins penetrate deeper into the pellet, the inner regions are also poisoned. As a result, a well-marked deactivation front is formed which poisons the whole catalyst by its inward progress [11].

Khang and Levenspiel [12] showed that the simple power law rate is applicable to the deactivating catalyst pellet when parallel first order fouling occurs, along with a first order gas-phase reaction in the strong pore diffusion limitation regime. Here, their analysis is extended to second order poisoning kinetics, in parallel with a first order main reaction, occurring in the liquid phase. Another extension of the present study is to include the effect of pore-mouth plugging in such analysis.

To account for the effects of diffusion, consider a single pore as shown in Figure 1. In the case of strong diffusion resistance, the progressive approximation of the shell, as described above, is applicable. Accordingly, the entire pore can be divided into two well-defined regions; a poisoned outer zone, which grows inwards and an inner active zone. The point activities are taken to be zero in the poisoned zone, while they are unity in the active zone.

The effect of diffusion on the main reaction can be simply accounted for by the well-known effectiveness factor [2], i.e.:

$$-r_B = k_A \eta_X \frac{X}{L} C_{BX}, \tag{5}$$

where $-r_B$ is the reaction rate per volume of the pore. As shown in Figure 1, L and X are the total length of the pore and active zone, respectively; C_{BX} is butene concentration at the entrance of the active zone and η_X is the effectiveness factor for the clean portion of the pore. The impact of diffusion on site poisoning, however, is more complicated. Because of the prevailing high diffusion limitation, the concentration decline in the active region is very sharp with concentration approaching zero very close to the poisoning front. Therefore, poisoning occurs almost exclusively at the deactivation front and a site balance over the entire

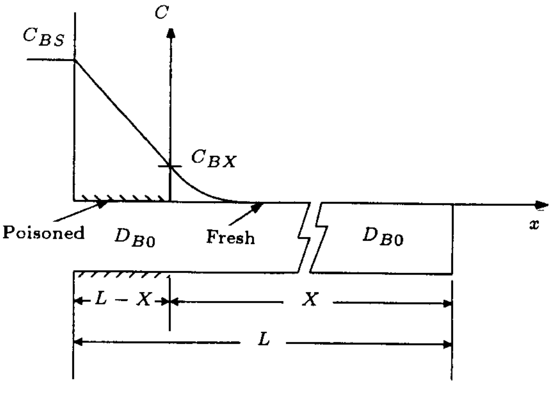


Figure 1. Schematic representation of the SPM in a pore in the absence of pore-mouth plugging.

active zone gives:

$$-\frac{dX}{dt} = \int_0^X k_P C_B^2(x)dx, \tag{6}$$

where $C_B(x)$ is the concentration profile in the clean region and the lower limit of the integral corresponds to the location of the deactivation front (i.e. entrance to the clean zone). The definition of catalyst activity [2] is given by:

$$\mathbf{a} = \frac{-r_B}{-r_{B0}}, \tag{7}$$

where **a** is the overall pellet activity and $-r_{B0}$ is the initial reaction rate. Equations 3 to 7 are used to obtain an expression for the overall catalyst deactivation as follows.

Decay Law

Because of the presumed high diffusion limitation, the semi-infinite slab approximation for the pellet is valid [12]. When the velocity of the diffusing reactant is high compared with the velocity of the poisoning front, the steady concentration profile for the reactants can be established. This is normally the case for gas-phase systems [13,14]. In the present case of liquid-phase alkylation, where the concentration of butene is assumed to be very low, this assumption is still valid.

The poisoning reactions may bring about an additional diffusional restriction in the poisoned zone by reducing the available cross-sectional area for the diffusing species. In the absence of such pore-mouth plugging effects, the effective diffusivity would be constant throughout the entire pore and equal to that for the clean portion (i.e. D_{B0}; see Figure 1). Otherwise, the effective diffusivity in the poisoned zone (i.e. D_P) would be smaller than that in the clean zone (i.e. $D_P < D_{B0}$; see Figure 2).

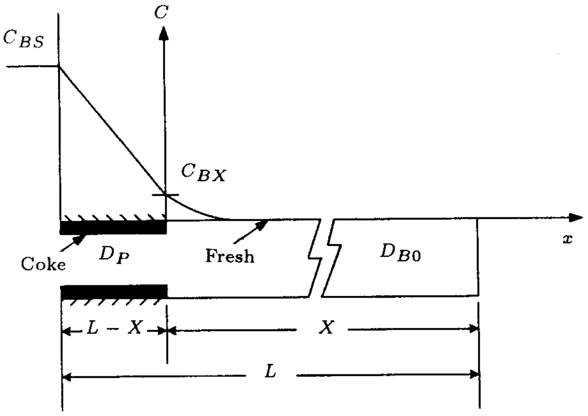


Figure 2. Schematic representation of the SPM in a pore in the presence of pore-mouth plugging.

In the case of constant diffusivity (Figure 1), assuming that the deposition of poison is negligible compared with the butene turnover (a reasonable assumption for a normal catalyst), the rate of butene transfer equals that of the reaction in the clean zone:

$$-r_B = \frac{D_{B0}}{L(L-X)}(C_{BS} - C_{BX}), \tag{8}$$

where C_{BS} is butene concentration at the pore entrance.

Eliminating C_{BX} from Equations 5 and 8, then substituting its value into Equation 5 results in the following expression:

$$-r_B = \frac{k_A X D_{B0} \eta_X / L}{D_{B0} + k_A X(L-X)\eta_X} C_{BS}. \tag{9}$$

For first order reactions, when $X = L$ (i.e. $t = 0$ or no deactivation), Equation 9 reduces to the following familiar form:

$$-r_{B0} = k_A \eta_L C_{BS}, \tag{10}$$

where η_L is the effectiveness factor based on the total pore length. Rearranging Equation 9 gives:

$$-r_B = \frac{D_{B0}}{\eta_L L} \frac{X\eta_X}{D_{B0} + k_A(L-X)X\eta_X} k_A \eta_L C_{BS}. \tag{11}$$

Now, from Equations 7, 10 and 11 one obtains:

$$\mathbf{a} = \frac{-r_B}{-r_{B0}} = \frac{D_{B0} X \eta_X / L\eta_L}{D_{B0} + k_A(L-X)X\eta_X}. \tag{12}$$

The effectiveness factor for a first order reaction in a clean cylindrical pore of length L is of the following form [2]:

$$\eta_L = \frac{\tanh mL}{mL}, \tag{13a}$$

where:

$$mL = L\sqrt{\frac{k_A}{D_{B0}}}. \tag{13b}$$

The dimensionless group, mL, is the Thiele modulus for a first order reaction. It is a measure of the importance of pore diffusion resistance. In a strong pore resistance regime, where $mL \geq 5$, Equation 13 simplifies to the following equation:

$$\eta_L \cong \frac{1}{mL}. \tag{13c}$$

Because of the semi-infinite slab approximation, one obtains:

$$L\eta_L = X\eta_X = \frac{1}{m}. \tag{14}$$

Combining Equations 14 and 8 results in:

$$\mathbf{a} = \frac{1}{1 + m(L - X)}, \tag{15a}$$

or:

$$L - X = \frac{1}{m}(\mathbf{a}^{-1} - 1). \tag{15b}$$

Equation 15 is applicable for any first order reaction, regardless of the poisoning kinetics, provided that the shell progressive mechanism is valid. It relates pellet activity to the penetration depth.

The particular kinetics for poisoning, given by Equation 4 and applied in Equation 6, may now be combined with Equation 15b to obtain the decay law. The steady concentration profile within a clean cylindrical pore of length L is known to be [2]:

$$\frac{C_B(x)}{C_{BS}} = \frac{\cosh m(L - x)}{\cosh mL}. \tag{16}$$

Inserting this profile (letting $L = X$ and $C_{BS} = C_{BX}$) into Equation 6, then, upon integration, one obtains:

$$-\frac{dX}{dt} = \frac{k_P C_{BX}^2}{2m \cosh^2 mX}\left[\frac{\sinh 2mX}{2} + mX\right]. \tag{17}$$

Noting that mX is very large (semi-infinite slab approximation and very high diffusional limitation), the above expression simplifies to the following:

$$-\frac{dX}{dt} = \frac{k_P C_{BX}^2}{2m}. \tag{18}$$

Next, combining Equations 5, 10, 14 and 18 will result in:

$$\begin{aligned}
-\frac{dX}{dt} &= \frac{k_P C_{BX}^2}{2m} = \frac{mk_P}{2}(X\eta_X C_{BX})^2 \\
&= \frac{mk_P}{2}\left(-\frac{Lr_B}{k_A}\right)^2 = mL^2 k_P \frac{(-r_{B0}\mathbf{a})^2}{2k_A^2} \\
&= mL^2 k_P \frac{(k_A \eta_L C_{BS}\mathbf{a})^2}{2k_A^2},
\end{aligned}$$

which, upon further algebraic manipulation, reduces to the following:

$$-\frac{dX}{dt} = \frac{k_P}{2m}C_{BS}^2 \mathbf{a}^2. \tag{19}$$

On the other hand, differentiation of Equation 15b yields:

$$-\frac{dX}{dt} = -\frac{1}{m}\mathbf{a}^{-2}\frac{d\mathbf{a}}{dt}. \tag{20}$$

Finally, from a combination of Equations 19 and 20, one obtains:

$$-\frac{d\mathbf{a}}{dt} = \frac{k_P}{2}C_{BS}^2 \mathbf{a}^4. \tag{21}$$

This last equation shows that the differential form of the decay (deactivation) rate law is second order in external (i.e. pellet surface) butene concentration and fourth order in terms of the pellet activity.

In the above formulation, the effect of the deposited carbonaceous materials on the pore surface and their impact upon the diffusion coefficient of the reactant was neglected. However, such an assumption is not necessarily the case, as the coke may be sufficient to create an extra diffusional resistance. Here, the derivative of the concentration profile within the pore is not a continuous function. It changes sharply at the boundary of the poisoned and active zones (Figure 2).

An analysis similar to that presented above may be used to obtain the decay law for this case. Only the form of Equation 8 alters, in which D_{B0} is replaced by D_P. Following the subsequent manipulations, one obtains:

$$L - X = \sqrt{\frac{D_p^2}{k_A D_{B0}}}(\mathbf{a}^{-1} - 1). \tag{22}$$

This equation is comparable with Equation 15b. Next, combining Equations 18 and 22, one obtains:

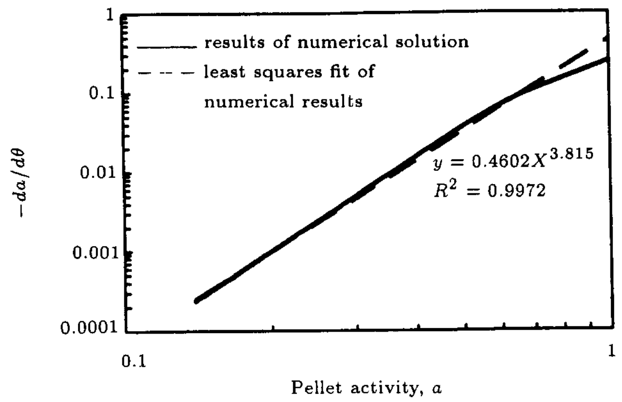
$$-\frac{d\mathbf{a}}{dt} = \frac{D_{B0}}{2D_P}k_P C_{BS}^3 \mathbf{a}^4. \tag{23}$$

Again, a fourth order decay law is obtained. For the special case that $D_P = D_{B0}$ (i.e. no pore plugging), Equation 23 reduces to Equation 21.

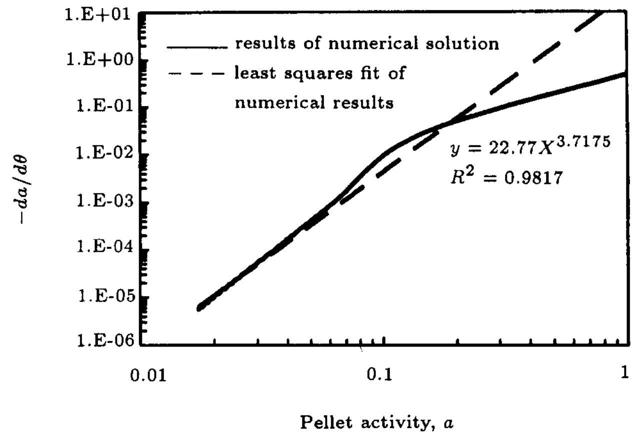
The analysis presented above clearly shows that diffusion has a great impact on the catalyst deactivation behavior in alkylation. When diffusion effects are negligible, the intrinsic rates of reaction and deactivation (Equations 3 and 4) suffice for describing the overall behavior of the pellet, provided that point activity and concentrations, are replaced by the overall activity and bulk concentrations, respectively. However, in the regime of strong pore diffusion limitation, which is the case for liquid-phase alkylation, the resultant differential form of the decay rate law is second order in external butene concentration and fourth order in overall activity. Although the occurrence of pore-mouth plugging enhances catalyst deactivation, it does not change the form of the decay law.

RESULTS AND DISCUSSION

The results of the preceding section can be confirmed by the numerical solution of the governing differential



a) $D_P/D_{B0} = 1$ (no pore-mouth plugging)



b) $D_P/D_{B0} = 0.01$

Figure 3. Deactivation rate versus pellet activity [15]; $mL = 200$ and $\theta = t.k_p.C_{BS}^2$ is the dimensionless time.

equations, which have been presented elsewhere [15]. Figure 3 represents the fitting of the numerical results with power law decay for the above two cases. In the later stages of deactivation, for both cases, the exponent of the power law decay approaches 4, in the limit of high diffusional resistances where the Thiele modulus approaches infinity. In the earlier stages of deactivation, however, a lower order of deactivation is observed for both cases. This is attributed to the fact that at the early stage, the characteristic S-shaped activity profile within the pore has not yet been fully established [12]. This deviation is more pronounced in the case of strong pore-mouth plugging effects, resulting in a lower average order of deactivation.

To check the validity of the decay law and to obtain an empirical value for the order of deactivation, one may use the method outlined by Levenspiel [2,16], given below. Since the reaction is strongly intraparticle diffusion limited, the bulk butene concentration may be considered to be the same as that on the catalyst surface, C_{BS}. Consequently, in the case of parallel deactivation for a batch of solids in a CSTR and at constant bulk butene concentration, the expressions for the apparent rates of the main and poisoning reactions become:

$$-r'_B = (k_a C_{BS})\mathbf{a} = k'_a\mathbf{a}, \tag{24}$$

$$-\frac{d\mathbf{a}}{dt} = (k_d C_{BS}^2)\mathbf{a}^d = k'_d\mathbf{a}^d, \tag{25}$$

where r'_B, is the rate of butene consumption per catalyst weight, d is the average order of deactivation and k_a and k_d are the apparent rate constants for the respective reactions. Applying Equation 24 into the performance equation of the back-mixed reactor gives:

$$\tau' = \frac{C_{B0} - C_{BS}}{k'_a\mathbf{a}}, \tag{26}$$

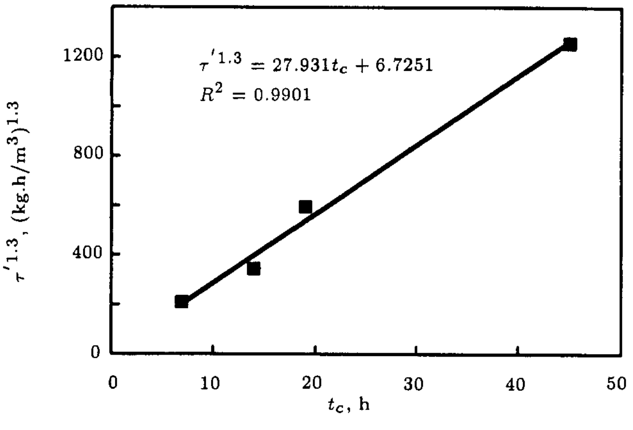
where $\tau' = W_c/\nu$ is a capacity factor for the reactor called the weight-time. Here, W_c and ν are the catalyst weight and feed volumetric flow rate, respectively. Next, integrating Equation 25 and, then, replacing into Equation 26 and rearrangment, gives [16]:

$$\begin{aligned}(\tau')^{d-1} &= \left(\frac{C_{B0} - C_{BS}}{k'_a}\right)^{d-1} \\ &+ \left(\frac{C_{B0} - C_{BS}}{k'_a}\right)^{d-1}(d-1)k'_d t \\ &= C_1 + C_2 t \qquad d \neq 1. \end{aligned} \tag{27}$$

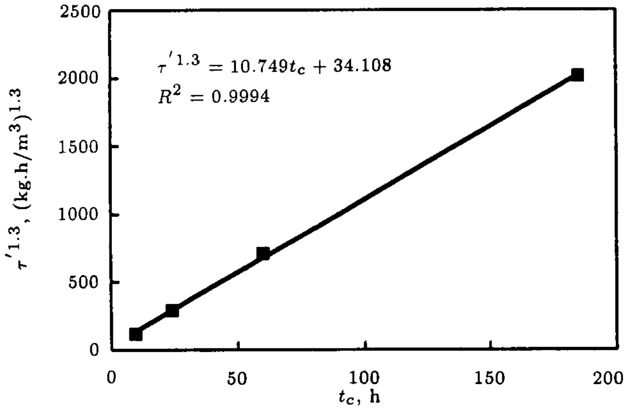
Therefore, one should guess a value for d and then plot $(\tau')^{d-1}$ versus t. If the data fall on a straight line, the guessed mechanism is correct. The use of the back-mixed mode as the medium for checking the decay law is consistent with the former assumption of very low butene concentration in the reaction zone utilized in the modeling.

Experimental data to fit Equation 27 are rarely available in the literature. However, the following approach may be employed to provide such data. Assume the case of constant feed concentration (C_{B0}) with variable weight-time (τ'). Now, the catalyst lifetime, t_c, is defined as the time required for the butene conversion to drop below 90% (i.e. $X_B = 0.9$). As such, at the end of the catalyst life, the bulk butene concentrations become identical and, therefore, C_1 and C_2 in Equation 27 remain constant for different experimental runs. Consequently, the above procedure is applicable to check the validity of the model and to determine d. Since the catalyst lifetime is used as the basis of this approach, the resultant, d, represents the time-averaged order of deactivation over the entire useful catalyst life. This may be considered as an advantage of this methodology.

Figure 4 shows the results of fitting Equation 27 with two sets of experimental data, using zeolites as the catalyst. They both show a good fit for a value



a) USHY zeolite, $c_{B0} = 0.17$ kgmol/m^3, $T = 367$ K (experimental data from [8])



b) Zeolite beta, $c_{B0} = 0.28$ kgmol/m^3, $T = 363$ K (experimental data from [10])

Figure 4. Experimental verification of the power law expression for catalyst deactivation.

of 2.3 for d. Therefore, 2.3 is an acceptable average order of deactivation. This value being considerably smaller than 4 implies that pore-mouth plugging plays an important role in deactivation of the catalyst in zeolite catalyzed alkylation (see Figure 3).

It is noteworthy that other researchers have arrived at the same conclusion through analyzing experimental observations. Querini and Roa [7] studied coke formation on a number of large-pored zeolites, as well as, sulfated zirconia in liquid-phase isobutane alkylation. From pore volume and surface area measurements carried out on the fresh and deactivated catalysts, a pore plugging mechanism was suggested for catalyst deactivation. Taking the conservative density of 0.8 g/cm^3 (corresponding to the density of light paraffinic hydrocarbons) for carbonaceous deposits, the volume occupied by these materials, in certain samples, was estimated to be 0.1 cm^3/g catalyst. Since the pore volume measured for the same sample was zero cm^3/g, it was concluded that the 0.21 cm^3/g pore volume measured for the fresh catalyst was not accessible, due to pore-mouth blockage in the deactivated catalyst. This may be viewed as an independent experimental verification of the occurrence of pore-mouth plugging as predicted by the present analysis.

Pore-mouth plugging effects become important in the case of microporous catalysts, such as zeolites, while such effects are expected to be less significant in the case of meso- or macroporous catalysts. Since most of the activity loss occurs in the early phases of deactivation, one should apply a decay rate expression with an exponent somewhat lower than four. This is especially the case for a catalyst with severe pore-mouth plugging effects, as was demonstrated by the numerical solution of the governing equations (Figure 3).

CONCLUSIONS

The application of the shell progressive mechanism to catalyst deactivation in liquid-phase alkylation showed that the prevailing diffusion limitation severely affects the deactivation behavior of the catalyst. This is mainly due to the lowering accessibility of active sites to the reactants. In the case of the deactivated catalyst, the poisoned zone provides an ever-increasing additional resistance to the reactants. Therefore, the observed reduction in activity is not directly due to the decrease of the total number of active sites; rather it is due to the lowering of the effectiveness factor. A fourth order decay law in catalyst activity was obtained in the regime of strong intraparticle diffusional limitations. In the case of severe pore-mouth plugging effects, the deactivation rate was enhanced inversely by the diffusion reduction factor, i.e. the ratio of diffusivity in the fouled pore to that of the clean pore.

A deviation from the 4th order decay is expected at the initial stage of deactivation, as the characteristic S-shaped profile of activity within the pore is not fully established. The occurrence of pore-mouth plugging enhances this deviation resulting in a lower average order of deactivation.

Using experimental catalyst lifetimes, an empirical order of deactivation of 2.3 was obtained for zeolites. This implies that pore-mouth plugging plays a significant role in zeolite catalyzed alkylation.

NOMENCLATURE

a	catalyst activity
A	alkylate
C	concentration (kgmol/m^3)
d	order of deactivation
D	diffusivity (m^2/s)
D	dimer
I	isoparaffin

k_A	pseudo-rate constant for alkylation reaction (s^{-1})
k_P	pseudo-rate constant for poisoning reaction ($m^6/kgmol^2.s$)
L	total pore length (m)
mL	Thiele modulus
O	olefin
$-r_B$	rate of butene consumption per catalyst volume ($kgmol/m^3.s$)
r_0	pellet radius (m)
t	time (s)
X	length of active zone (m)

Greek Symbols

α	point activity
η	effectiveness factor
θ	dimensionless time
ρ	density (kg/m^3)
τ'	weight-time ($kg.h/m^3$)

Subscripts

B	of butene
P	poisoning
S	surface
0	entering or initial condition

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