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Evaluation of Modes of Catalyst Deactivation by Coking for Cumene Cracking over Zeolites

A. BELLARE[1] AND D. B. DADYBURJOR[2]

Department of Chemical Engineering, West Virginia University, Morgantown, West Virginia 26505-6101

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The deposition of coke deactivates a catalyst by the suppression of active sites and/or by choking of pores. The so-called Constant-Coke Arrhenius Plot technique can assess the magnitudes of these two modes of deactivation using reaction experiments under process conditions. For cumene cracking over REY zeolite, a TGA has been used as a continuous-flow microreactor to monitor coke levels, with activity measured by an on-line GC. Using modifications described previously for small-pore catalysts, we show that both temperature and coke level influence the relative importance of site suppression and pore choking in the deactivation of the zeolite. At relatively high temperatures, site suppression is predominant at all coke levels studied here. At lower temperatures, pore choking is more important at low levels of coke, with site suppression increasing in importance at the higher coke levels. The results are consistent with a physical model developed.

INTRODUCTION

Deactivation of cracking catalysts due to coking (or poisoning) is known to occur by two mechanisms: active site suppression and pore choking. In the case of active site suppression, the coke (poison) molecules are irreversibly adsorbed on the active sites of the catalysts, in particular, on those sites that are required for the main catalytic reaction, leading to a decrease in the catalytic activity. In pore choking, the coke (poison) molecules are adsorbed on the walls of the pores, thereby increasing the diffusional resistance in the pore, and again the catalytic activity decreases as a consequence. In general, active site suppression and pore choking can occur simultaneously during coking and/or poisoning of cracking catalysts. However, one of the two mechanisms may be predominant.

Several researchers have attempted to identify the predominant mechanisms of deactivation of catalysts during coking. Langner (*1*) studied the cracking of propylene over $NaNH_4$–Y zeolite catalyst at different temperatures, and related the loss of catalytic activity during deactivation to the decrease in catalyst pore volume. Langner concluded that, at reaction temperatures below 300°C, the deactivation is caused by coke precursors that are strongly adsorbed on some of the active sites in the pores. However, at high temperatures, the coke is formed on the exterior surface of the catalyst, causing pore mouth blockage.

Stephens and Stohl (*2*a,b) studied the deactivation mechanisms in coal liquefaction catalysts by determining the intrinsic rate constant and effective diffusivity values during the catalytic hydrogenation of pyrene on a nickel-molybdate-on-alumina catalyst. They concluded that deactivation of the catalyst takes place by two mechanisms: the metal contaminants in the coal liquids cause irreversible pore mouth blocking, and the coking taking place during reac-

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[1] Present address: Union Carbide Chemicals & Plastics Company, Inc., P.O. Box 670, Bound Brook, NJ 08805.

[2] To whom correspondence should be addressed.

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tion suppresses the active sites on the catalyst.

Other researchers have used indirect techniques to estimate the values of the intrinsic rate constants and effective diffusivities to predict catalyst deactivation mechanisms. Bulow *et al.* (*3*) used a probe molecule, methane, to estimate the effective diffusivity of *n*-hexane in coked and fresh HZSM-5 zeolites. Pyridine chemisorption was used to obtain the number of active sites in fresh and coked samples. Bulow *et al.* suggested that both active site suppression and pore choking take place during coking, and the mode of deactivation is dependent on the relative sizes of the catalyst pores and the reactant molecule. Solinas *et al.* (*4*) studied the mechanism of coke deposition on Y-zeolites during isomerization of methylnaphthalene and, from the relative rates of the coking and isomerization reactions as a function of time on stream, concluded that active site suppression is the predominant mechanism of deactivation in Y-zeolites. Magnoux and co-workers (*5*) have conducted an extensive study of the mechanisms of deactivation of several different zeolite catalysts during *n*-heptane cracking. Using adsorption isotherms of nitrogen and *n*-hexane to determine pore volumes of the fresh and coked catalyst, experimentally determining the effective diffusivity of *n*-hexane, and estimating the number of active sites of coked and fresh catalysts by ammonia chemisorption, Magnoux *et al.* determined whether pore choking or active site suppression occur during coking of HY, HM, USHY, and HZSM-5 zeolites. On HM and USHY zeolites, deactivation occurs by pore blockage even at coke levels of 1% by weight. However, on HZSM-5 zeolites, deactivation occurs initially due to active site suppression and later by pore mouth blocking.

However, a major drawback in all of these is the indirect approach used to obtain information on active site suppression and pore choking. In order to estimate intrinsic rate constants and effective diffusivities of reactants during the process of deactivation of the catalyst, researchers have used methods like catalyst crushing and probe molecules. Due to the likelihood of significant errors being introduced during extrapolation of these parameters to the conditions of the reaction, the use of indirect methods to determine the predominant mode of deactivation can be misleading.

In this work, the Constant-Coke Arrhenius Plot (CCAP) is modified and used to examine the relative importance of active site suppression and pore choking during catalyst deactivation for cumene cracking over REY zeolite. The CCAP technique is quantitative and allows the intrinsic rate constant and the effective diffusivity of the reactants to be evaluated as a function of the extent of deactivation of the catalyst under the conditions of the reaction. Due to its relevance in this work, the CCAP technique used here is described below.

CONSTANT-COKE ARRHENIUS PLOTS

The basic technique (*6*) is a modification of Ref. (*7*) and evaluates the intrinsic rate constants (k_{int}) and the effective diffusivities (D_{eff}) of the reactant–zeolite system under actual reaction conditions and at different extents of catalyst deactivation. The change in the magnitude of the intrinsic rate constant, as a function of the deactivation of the catalyst, can then be related to the suppression of active sites during catalyst deactivation. On the other hand, the change in the effective diffusivity of the reactant, as a function of the deactivation of the catalyst, indicates the phenomenon of pore choking during catalyst deactivation. From the relative changes in the magnitudes of the intrinsic rate constants and effective diffusivities of the reactant during catalyst deactivation, it is possible to predict the relative importance of active site suppression and pore choking during deactivation of the catalyst.

The evaluation of k_{int} and D_{eff} under the conditions of the reaction is not trivial, since they are coupled through the effectiveness factor and the Thiele modulus. Moreover, the catalyst activity data, such as conversions at various times on stream, can only be used to calculate the observed rate constant (k_{obs}) rather than the intrinsic rate constants (k_{int}).

The CCAP technique consists of obtaining the first-order observed rate constant (k_{obs}) and the coke level of the catalyst (C) at different times on stream for a wide range of temperatures, from very low to high temperatures. Arrhenius plots are constructed, each at different but constant extents of deactivation (C). Two asymptotes can be drawn to each constant-coke Arrhenius plot, one each at the low- and the high-temperature regions. The equations for computing the intrinsic rate constants and effective diffusivities can be derived from the slopes and the intersection point of the low-temperature and high-temperature asymptotes on the constant-coke Arrhenius plots. For details, see Ref. (*6*). The equations for the intrinsic rate constants, k_{int}, and the effective diffusivities of the reactant, D_{eff}, are developed from the conventional steady-state equation for diffusion and reaction in a catalyst pore,

$$k_{\mathrm{int}}(C,T) = k_x(C)\exp[-m_L(C)/T_x(C)] \exp[m_L(C)/T] \quad (1a)$$

$$= A_L(C,T) \quad (1b)$$

$$D_{\mathrm{eff}}(C,T) = l^2\rho k_x(C) \exp[(m_L(C) - 2m_H(C))/T_x(C)] \times \exp[-(m_L(C) - 2m_H(C))/T] \quad (2a)$$

$$= \frac{l^2\rho A_H^2(C,T)}{A_L(C,T)}, \quad (2b)$$

where k_x and T_x represent the location of the intersection point of the two asymptotes; m_L and m_H are the slopes of the low-temperature and high-temperature asymptotes, respectively. $A_L(C, T)$ and $A_H(C, T)$ are the values of the low-temperature and high-temperature asymptotes, respectively, at coke level C and temperature T. In Eq. (2), l is the characteristic length parameter, and ρ is the bulk density, of the catalyst particle.

A_L and A_H are given by the equations

$$A_L = m_L(C)/T + I_L \quad (3a)$$

$$A_H = m_H(C)/T + I_H, \quad (3b)$$

where I_L and I_H are the intercepts of the low-temperature and high-temperature asymptotes, respectively. An important point to note here is the relationship between m_L and m_H. These slopes are related to the activation energies of reaction, E_{int}, and diffusion, E_d. In conventional catalyst systems, E_d is significantly smaller than E_{int}. Therefore, m_H, is almost equal to, but slightly greater (in absolute magnitude) than, one-half the slope of the low-temperature asymptote, m_L, i.e.,

$$m_H \geq m_L/2. \quad (4)$$

The technique presented above is based on the mechanisms of diffusion and reaction in deactivating conventional catalysts. In smaller-pore catalyst systems like REY zeolites, the critical diameter of the reactant molecule is of the same order of magnitude as the size of the pores. A free gas phase may be absent within the pores of such catalyst systems: instead, a condensed-type phase may be present at the external surface of the zeolite and within the catalyst pores. The sequence of the reaction in such catalyst systems is postulated to be as follows: "condensation" of the reactant from the gas phase as a condensed phase on the external surface of the catalyst; diffusion of the reactant along the pore walls, perhaps analogous to surface diffusion, followed by reaction at the active site, and the diffusion of the products to the external surface of the catalyst; and finally, the "evaporation" of the products from the condensed phase to the gas phase. Such a reaction model has been also advanced elsewhere (*8*, *9*). Using the model described above, the following expressions can be derived for the intrinsic rate constant and effective diffusivity (*10*):

$$k_{\mathrm{int}}(C,T) = \frac{k_x(C)\exp[m_L(C)(1/T - 1/T_x)]}{\rho K_0 \exp[-\Delta H_{\mathrm{ads}}/RT]} \quad (5a)$$

$$= \frac{A_L(C, T)}{\rho K_{ads}(C, T)} \tag{5b}$$

$$D_{eff}(C, T)$$

$$= \frac{\{l^2 k_x(C) \exp[(2m_H(C) - m_L(C))(1/T - 1/T_x)]\}}{K_0(C) \exp[-\Delta H_{ads}/RT]} \tag{6a}$$

$$= \frac{l^2 A_H^2(C, T)}{A_L(C, T) K_{ads}(C, T)}. \tag{6b}$$

For these small-pore catalyst systems, the observed activation energies have a term for the enthalpy of adsorption, ΔH_{ads}, due to the consideration of the process of "condensation" before diffusion and reaction in the catalyst. Therefore, in the Arrhenius plot, the slope of the low-temperature asymptote, m_L, and the slope of the high-temperature asymptote, m_H, are given by

$$m_L = \frac{-(E_{int} + \Delta H_{ads})}{R} \tag{7a}$$

$$m_H = \frac{-(E_{int} + E_d + 2\Delta H_{ads})}{2R}. \tag{7b}$$

Equations (7) indicate that the slope of the high-temperature asymptote, m_H, in the Arrhenius plot will always be significantly smaller than one-half the slope of the low-temperature asymptote, m_L, for high values of ΔH_{ads}. This suggests that whenever this effect is important (the magnitude of ΔH_{ads} is high) during diffusion and reaction in small-pore catalyst systems like zeolites, the slope of the high-temperature asymptote will always be much smaller (in absolute magnitude) than one-half the slope of the low-temperature asymptote. The breakdown of the relationship between the high-temperature and low-temperature asymptotes of Eq. (4) may be a criterion for determining whether "condensation" effects are important during diffusion and reaction in small-pore catalyst systems.

The CCAP technique, modified as in Eqs. (5)–(7), can be used to evaluate the intrinsic rate constants and effective diffusivities as a function of coke on a zeolite under reaction conditions. The relative magnitudes of the intrinsic rate constants and the effective diffusivities can then be used to determine the predominant mechanism of coking. The procedure for obtaining data for this purpose is described below.

EXPERIMENTAL

Cumene cracking over rare-earth-exchanged Y (REY) zeolite was used in this study. The REY zeolite, obtained from W. R. Grace, had a particle size of 1 μm with a pore diameter of 9 Å. The zeolite contains 0.88% (by weight) residual Na_2O and has a specific surface area of 620 m^2/gm.

The experimental setup consists primarily of a cumene reservoir, a thermogravimetric analyzer (TGA), and a gas chromatograph (GC) (Fig. 1). The Cahn System 113-DC TGA microreactor equipped with a Cahn 2000 Recording Electrobalance was used to carry out the cumene cracking reaction. The electrobalance was interfaced with a data acquisition system to obtain the weight of coke on the catalyst. The conversion of cumene during cracking was determined online by a Varian 3700 GC. Flowrates were adjusted such that conversions were kept relatively low, generally less than 15%.

Due to the low partial pressure of cumene used, the only major products were benzene and propylene. Contrary to the results of Best and Wojciechowski (*11*), no other major cracking products, due to disproportionation or any other second-order (bimolecular) reactions, were obtained in any significant quantities. In addition, there was no evidence of an *n*-propyl benzene peak in the chromatograms, indicating that the isomerization was not significant in the cracking experiments.

The experiments were performed at different temperatures and different times on stream. From each experiment, plots of conversion of cumene as a function of time, and coke on the catalyst as a function of time, were obtained. Combining these data from each experiment allows us to generate plots

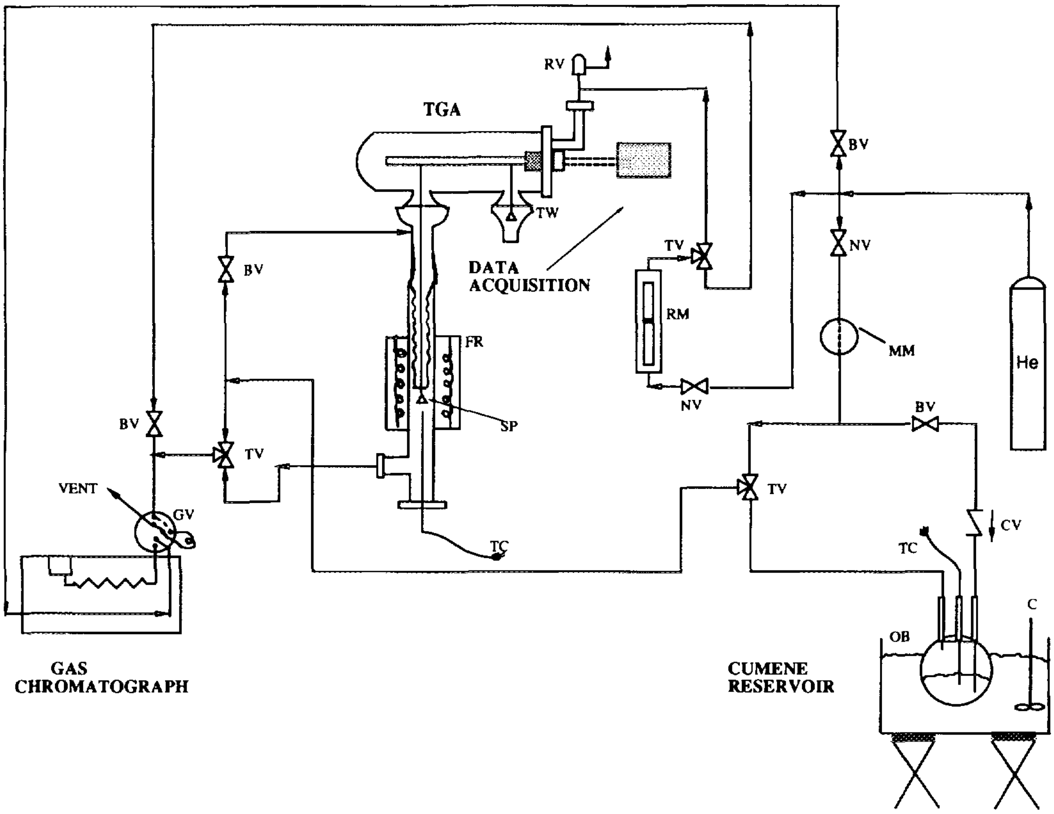

FIG. 1. Cumene cracking reaction apparatus: (BV) ball valve, (C) circulator, (CV) check valve, (FR) furnace, (GV) gas sampling valve, (MM) mass flowmeter, (NV) needle valve, (OB) oil bath, (RM) rotameter, (RV) relief valve, (SP) sample pan, (TC) thermocouple, (TV) three-way valve, and (TW) tare weights.

of cumene conversion as a function of coke on the catalyst at the different reaction temperatures and different times on stream. Figure 2 shows a representative plot of cumene conversion versus coke on catalyst at a reaction temperature of 350°C, a cumene molar feed rate of 1.7×10^{-4} mol/min, and 13 mg of REY zeolite.

RESULTS AND DISCUSSION

Constant-Coke Arrhenius Plots

In a TGA, a significant amount of gas flow bypasses the sample pan containing the catalyst. For our apparatus, f, the fraction contacting the sample has been determined to be approximately 0.4 (*12*). Hence the rate constant calculated from the observed conversion is, in principle, nonlinearly dependent on the actual observed rate constant in the absence of the bypass. However, at the low conversions considered here, the two rate constants are related by a constant factor (f^2). Hence the calculated first-order observed rate constants were directly obtained from Fig. 2 and similar plots. The observed first-order rate constants at each coke level were calculated using data from four cracking experiments at two different space times.

The relative magnitudes of the observed rate constants at temperatures of 225, 250, 500, and 575°C are plotted in Fig. 3, as a function of coke on the catalyst. At the low temperatures, the observed rate constant at

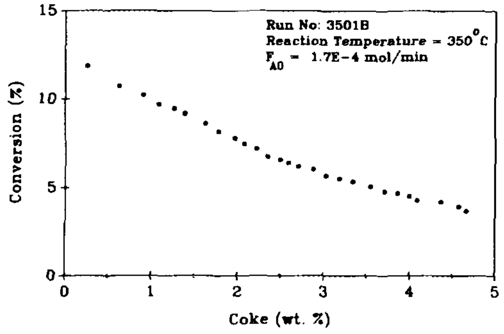

FIG. 2. Plot of cumene conversion during cracking on REY zeolite at 350°C as a function of coke on catalyst.

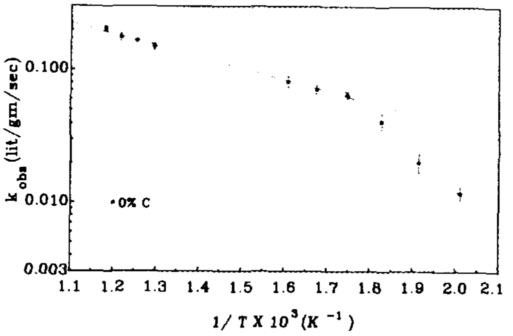

FIG. 4. Arrhenius plot for fresh REY zeolite showing the low- and high-temperature asymptotes (*10*).

4% coke decreases to 40% of that for the fresh catalyst. However, at temperatures higher than 500°C, the observed rate constant decreases by only about 15% after 4% coke on the catalyst. In addition, at temperatures higher than 500°C, the plots in Fig. 3 indicate a linear relationship between the relative magnitude of the observed rate constants and the amount of coke on the catalyst. However, at lower temperatures, the linear relationship is not valid.

Figures 4–6 represent Arrhenius plots, each at different, constant, coke levels. At low coke levels, less than 3%, the transition from the intrinsic kinetic-controlled regime to a regime with strong diffusion effects is very abrupt. Similar results have been reported by Wan (*7*), who notes that the sharp transition is due to the regular pore structure found in zeolites. At the higher coke levels, the transition from one regime to the other appears to be more gradual. Further, with increasing coke levels up to 2%, the intersection point of the low-temperature and high-temperature asymptotes in the Arrhenius plots decreases slightly; at higher coke levels, the intersection point shifts to higher temperatures.

Activation Energies for Reaction and Diffusion

For the fresh catalyst, it can be seen from Fig. 4 that the value of m_H is −1989 K, whereas the value of m_L is −6620 K. The slope of the high-temperature asymptote, m_H, is significantly smaller (in absolute magnitude) than one-half the slope of the corre-

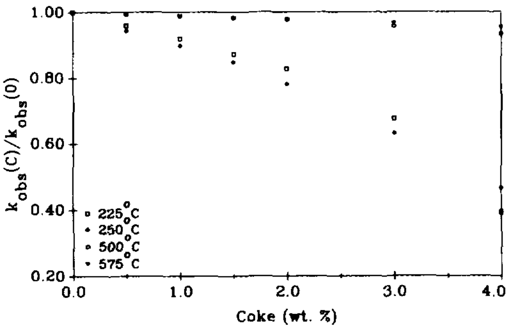

FIG. 3. Plot of the relative decrease in the observed rate constants as a function of coke on the catalyst (*19*).

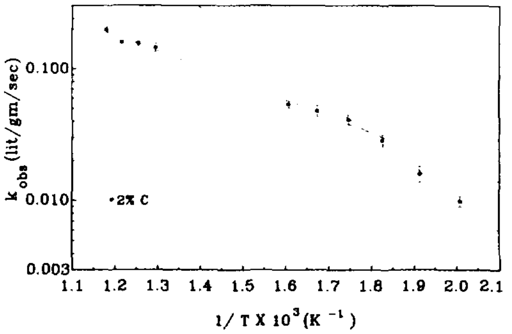

FIG. 5. Arrhenius plot for REY zeolite with 2.0% coke showing the low- and high-temperature asymptotes.

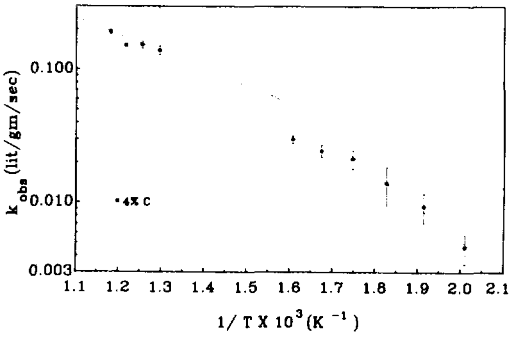

FIG. 6. Arrhenius plot for REY zeolite with 4.0% coke showing the low- and high-temperature asymptotes.

sponding low-temperature asymptote, m_L. This is attributed to the small-pore effects accompanying the process of diffusion and reaction of cumene on REY zeolites, as discussed above.

The activation energies E_{int} and E_d are calculated from Equations (7). The value of ΔH_{ads} for cumene adsorption on Y zeolites, is taken to be −20 kcal/mol (*13*). From these values, E_{int} for the fresh catalyst is calculated to be 33 kcal/mol, and E_d is 15 kcal/mol. The value of the activation energy for reaction is consistent with the values reported in the literature (*14*). The value of the activation energy for diffusion is high, but Satterfield (*15*) notes that high values are to be expected in zeolites due to their small pore sizes. A recent collection of data (*16*) lists values of 7 and 21 kcal/mol for benzene and dimethyl naphthalene respectively over analogous zeolites.

For the deactivated catalyst, E_{int} and E_d values are calculated in a similar fashion for all coke levels up to 4%. Figure 7 is a plot of the activation energies as a function of coke on the catalyst. It can be seen that the activation energy for the reaction does not change appreciably with coke on the catalyst, suggesting that the mechanism of the cracking reaction is unaffected by the coking process. The activation energy for diffusion increases from 15 kcal/mol (for the fresh catalyst) to 20 kcal/mol (at 2% coke) on the catalyst, after which it levels off.

In the calculations leading to Fig. 7, the enthalpy of adsorption, ΔH_{ads}, is assumed to be independent of coke level. This assumption may not be valid, since the enthalpy of adsorption of cumene on carbon is much smaller (in absolute magnitude) than the enthalpy of adsorption of cumene on Y-zeolite. The enthalpy of adsorption of cumene on graphitized carbon black is reported to be −12.3 kcal/mol (*17*). Therefore, the enthalpy of adsorption, ΔH_{ads}, may be a function of coke on the catalyst, and the value of ΔH_{ads} at higher coke levels may be smaller (in absolute magnitude) than −20 kcal/mol. With such a dependence of ΔH_{ads} on coke levels, Eqs. (7) indicate that the activation energy for reaction would tend to level off while that for diffusion would tend to increase still further. It is reasonable to expect, therefore, that changes in the activation energy of reaction with coke level are small, while the activation energy of diffusion increases with coke level.

Intrinsic Rate Constants and Effective Diffusivities

The intrinsic rate constants and effective diffusivities were calculated using Eqs. (5) and (6) at coke levels from 0 to 4% at three reaction temperatures. The value of ΔH_{ads} was assumed to be −20 kcal/mol, indepen-

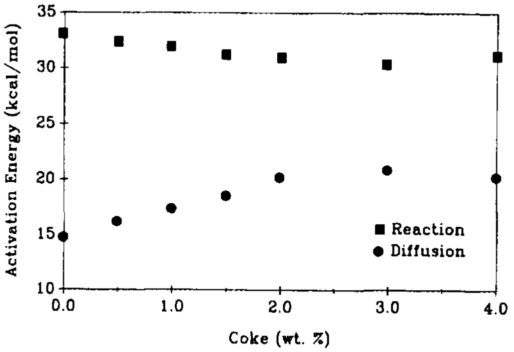

FIG. 7. Plot of activation energies for reaction and diffusion during cumene cracking on REY zeolites as a function of coke on catalyst.

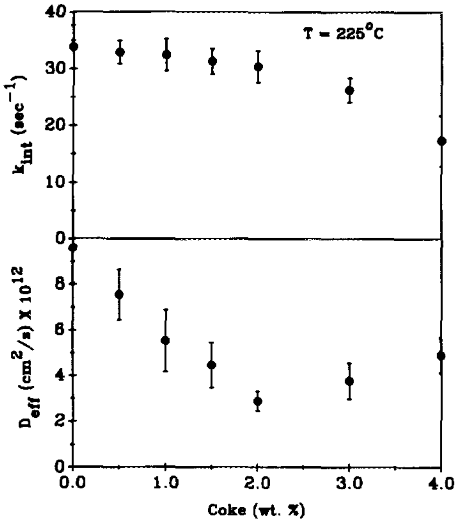

FIG. 8. Plot of intrinsic rate constants and effective diffusivities at 225°C as a function of coke on the catalyst (enthalpy of adsorption is assumed to be constant).

dent of coke level. The effect of decreasing the heat of adsorption with coke formation on the catalyst is described later.

Figure 8 is the plot of the intrinsic rate constants and effective diffusivities as a function of coke on the catalyst at a reaction temperature of 225°C. When up to 2% coke is deposited on the catalyst, the intrinsic rate constants do not show an appreciable decrease. However, from coke levels of 2 to 4%, the intrinsic rate constant decreases considerably. On the other hand, the effective diffusivity of cumene in the zeolite decreases sharply initially, i.e., up to 2% coke on the catalyst. At higher coke levels, the effective diffusivity appears to increase, although the increase is almost negligible when the error bars are taken into account. (The assumption of a constant value for ΔH_{ads} may also play a role; this and other possibilities are discussed later in this subsection.) Recall that a decrease in the intrinsic rate constant, and no change in the effective diffusivities, with increasing coke level, implies that active site suppression is the predominant mode of deactivation; while a decrease in the effective diffusivities, and no change in intrinsic rate constants, with increasing coke levels implies that pore choking is the predominant mode of deactivation. Then these results suggest that at 225°C, the predominant mechanism of deactivation changes with coke level: pore choking at coke levels below 2% and active site suppression between coke levels between 2 and 4%.

For the reaction at 350°C, the intrinsic rate constants and effective diffusivities are plotted in Fig. 9 as a function of coke on the catalyst. The intrinsic rate constant monotonically decreases as a function of coke on the catalyst. However, the effective diffusivity remains constant up to 2% coke on the catalyst, after which it shows a small increase. Again, the increase may be nullified by considering the error bars, or it may be a result of assuming that the heat of adsorption is not a function of coke on the catalyst. Therefore, at 350°C, active site suppression seems to be the predominant mechanisms of deactivation at all coke levels.

Figure 10 is a plot of the intrinsic rate constants and effective diffusivities at 500°C

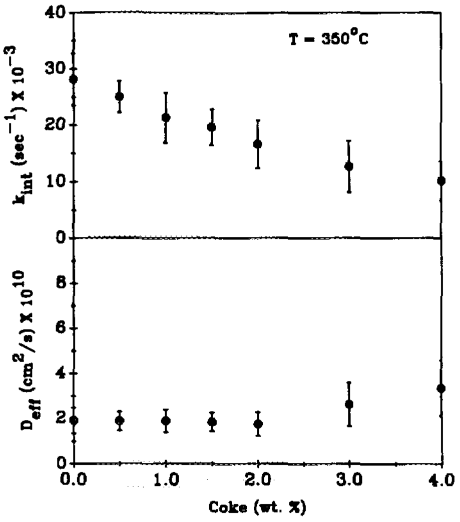

FIG. 9. Plot of intrinsic rate constants and effective diffusivities at 350°C as a function of coke on the catalyst (enthalpy of adsorption is assumed to be constant).

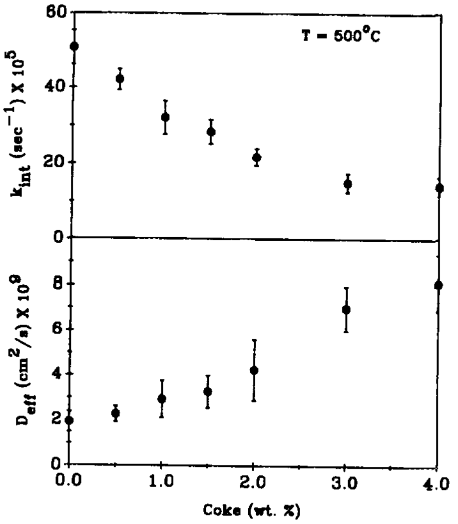

FIG. 10. Plot of intrinsic rate constants and effective diffusivities at 500°C as a function of coke on the catalyst (enthalpy of adsorption is assumed to be constant).

for different coke levels. The value of the intrinsic rate constant shows a monotonic decrease similar to the plot in Fig. 9. This suggests that active site suppression is significant at 500°C. However, the effective diffusivities appears to show an increase with coke on the catalyst. This may be attributed to the assumption of a constant enthalpy of adsorption. An alternative explanation is described in a later subsection.

To determine the magnitudes of the effect of the assumption of a constant heat of adsorption, the calculations were repeated assuming a decrease in the heat of adsorption value at a rate of 0.5 kcal/mol for every 1 wt% coke on the catalyst. In other words, the calculations for the intrinsic rate constant and effective diffusivity at 1% coke were performed using a value of heat of adsorption of 19.5 kcal/mol rather than 20 kcal/mol used for the case of the fresh catalyst (0% coke) and so on. Figures 11a, 11b, and 11c are the corresponding plots of the intrinsic rate constants and effective diffusivities at 225, 350, and 500°C respectively, as a function of coke on the catalyst. On comparing Fig. 10 and 11c, it can be seen that the shape of the plot remains essentially unchanged, although the magnitude of the intrinsic rate constant at each coke level has decreased. However, the effective diffusivity shown in Fig. 11c no longer increases with increasing coke levels. Clearly, even a very small change in the value of ΔH_{ads} with adsorbed coke can explain the apparent increase in the effective diffusivity with increasing coke levels. Hence, it may reasonably be expected that the diffusion coefficient does not increase in Figs. 8–10 but rather stays constant in these regions.

Another possibility to account for the increasing effective diffusivities in Figs. 8–10 is that the asymptote lines for the higher coke levels, e.g., in Fig. 6, are incorrectly drawn. However, we have shown elsewhere (*18*) that it does not appear possible to construct the high-temperature asymptote differently. This suggests that the increasing effective diffusivity values are more likely due to a result of assuming a constant enthalpy of adsorption than due to errors involved in constructing the high-temperature asymptote.

It is possible to analyze our data without making any assumptions about the nature of the heat of adsorption. From Eqs. (5) and (6), note that

$$\frac{k_{\mathrm{int}}(C, T)/k_{\mathrm{int}}(0, T)}{D_{\mathrm{eff}}(C, T)/D_{\mathrm{eff}}(0, T)} = \frac{\exp[(2m_{\mathrm{L}}(C) - 2m_{\mathrm{L}}(0))(1/T - 1/T_{x})]}{\exp[(2m_{\mathrm{H}}(C) - 2m_{\mathrm{H}}(0))(1/T - 1/T_{x})]} \qquad (8a)$$

$$= \frac{A_{\mathrm{L}}^{2}(C, T)A_{\mathrm{H}}^{2}(0, T)}{A_{\mathrm{L}}^{2}(0, T)A_{\mathrm{H}}^{2}(C, T)}. \qquad (8b)$$

The left hand side of Eq. (8) is the ratio of the relative change in the magnitude of the intrinsic rate constants, $k_{\mathrm{int}}(C, T)/k_{\mathrm{int}}(0, T)$, and effective diffusivities, $D_{\mathrm{eff}}(C, T)/D_{\mathrm{eff}}(0, T)$. This ratio has been termed R in preliminary work described elsewhere (*19*). R is a measure of the relative importance of pore choking relative to active site suppression. Note that the right-hand side of Eq. (8a) is not a function of the heat of adsorption, ΔH_{ads}, and hence R can be calculated di-

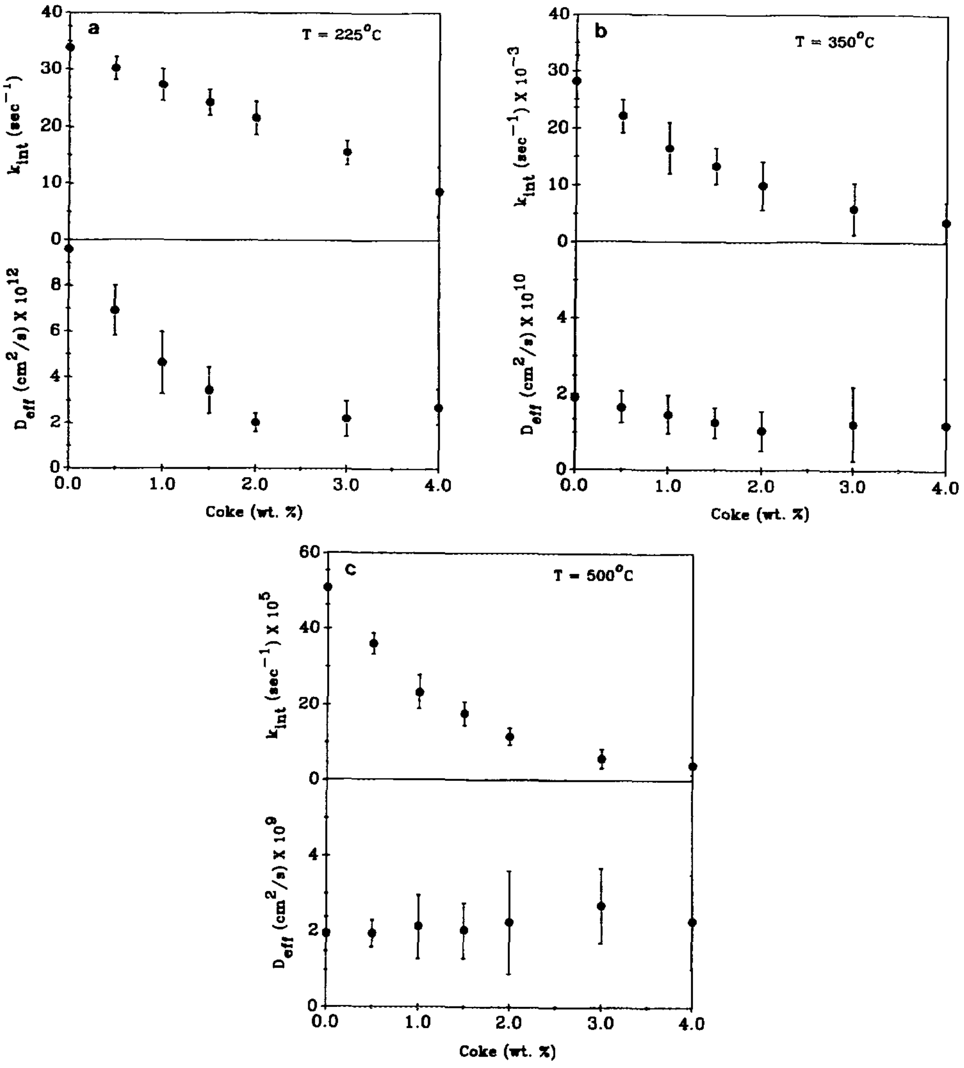

FIG. 11. Plot of intrinsic rate constants and effective diffusivities as a function of coke on the catalyst. The value of ΔH_{ads} is adjusted as described in text: (a) 225°C, (b) 350°C, and (c) 500°C.

rectly from the asymptotes. The conclusions drawn from Eq. (8) regarding the relative importance of active site suppression and pore choking are independent of whether the heat of adsorption, ΔH_{ads}, is assumed to be a function of coke or assumed constant.

In Fig. 12, we plot R as a function of the coke level at different temperatures. At 225°C, the abscissa increases from an initial value of 1 to a value of nearly 3 at about 2% coke, before it starts decreasing. Therefore, at 225°C, pore choking is the predominant mode of deactivation up to 2% coke on the catalyst. At coke levels higher than 2%, the value of the abscissa starts decreasing, indicating that active site suppression becomes more significant at higher coke levels. Therefore, it can be concluded that at 225°C, pore choking rather than active site suppres-

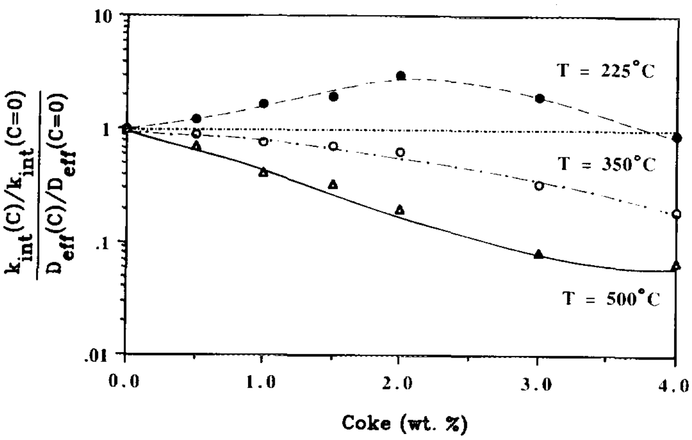

FIG. 12. Ratio R (relative decrease in the intrinsic rate constants to the decrease in the effective diffusivities) as a function of coke level (*19*).

sion is the predominant mechanism at coke levels below 2%; at higher coke levels, active site suppression becomes more important. These results are independent of the dependence of ΔH_{ads} on coke level.

At 350°C, the value of the abscissa is close to 1 up to 2% coke. This suggests that active site suppression and pore choking are approximately equally important in the region up to 2% coke. However, at coke levels higher than 2%, the abscissa decreases. This suggests that active site suppression is the predominant mechanism of catalyst deactivation in this range.

The plot in Fig. 12 for 500°C shows that the abscissa decreases monotonically, from a value of 1 for the fresh catalyst to a value of nearly 0.07 at 4% coke on the catalyst. This indicates that the predominant mechanism of deactivation of the REY zeolite at 500°C and at all coke levels is active site suppression. In addition, the abscissa in the plot at 500°C has a lower value at all coke levels when compared with the values at 350°C. Therefore, it can be concluded that at 500°C, active site suppression is more significant than at 350°C. In other words, for a given amount of coke on the catalyst, more active sites are suppressed at 500°C than at 350°C, and fewer pores are choked at the higher temperature.

Physical Model

We suggest the following physical model of cumene cracking over a coking catalyst as one which is consistent with the results of the previous subsection.

At low temperatures, the overall rate of the reaction is controlled by the intrinsic kinetics of the cumene cracking reaction rather than by the adsorption of cumene on the zeolite surface or by the diffusion of cumene into the pores of REY zeolite. This is because the adsorption of cumene on the zeolite surface and the diffusion of cumene into the pores are much faster than the intrinsic rate of the cumene cracking reaction at the lower temperatures. Therefore, at short times on stream, the cumene molecules are able to adsorb on the zeolite catalyst surface and to diffuse into the pore before any reaction occurs. As a result, coke is preferentially formed in the zeolite pores, causing the pores to get choked. However, at longer times on stream, it becomes more difficult for the cumene molecules to diffuse into some of the pores, as a result of pore choking. At this stage, when the catalyst has about 2% coke, some cumene molecules react on the catalyst surface rather than in the pores. This results in the suppression of the active sites at the larger stages of the reaction.

At higher temperatures, the overall rate of the reaction is more strongly influenced by the diffusion of the cumene molecules into the pores than by the intrinsic kinetics of the cracking reaction. At these higher temperatures, the intrinsic rates of the cumene cracking reaction are very high, compared to the rate of diffusion of cumene into the pores of the zeolite. This is due to a relatively small activation energy of diffusion compared to that of reaction. As a result of the slow diffusion process, the cumene molecules react very rapidly on the catalyst surface, even before the molecules can diffuse into the pores. As such, the reaction occurs primarily on the active sites located on the surface of the zeolite rather than inside the pores. Therefore, the deactivation of the catalyst is primarily due to the suppression of active sites on the catalyst surface. At high temperatures, it follows that the pores of the zeolite are not likely to be choked even at low coke levels, since most of the reaction occurs at the zeolite surface. The results of the present work indicate that, for coke levels up to 4%, there is no pore choking at the higher temperatures.

Comparison with Literature Results

The experimental results of the present study compare very well with the results of the "random walk" model of Theodorou and Wei *(20)* for the diffusion of molecules in zeolites. Here the zeolite catalyst is modelled as a 21 × 21 two-dimensional grid of intersecting pores, and the diffusion of the molecules as a succession of discrete jumps from intersection to intersection on the two-dimensional grid. Surface diffusion of the molecule within the zeolite crystal is also considered, by allowing lateral movement of molecules from site to site along the grid border. The model predicts that the observed rate constant decreases linearly as the active sites are blocked. In the present study, the observed rate constants decrease linearly with coke on the catalyst at the high temperatures, when active site suppression is the predominant mechanism of deactivation of the catalyst (Fig. 3). The model further predicts that, when the predominant mechanism of deactivation in zeolites is by the bulk blocking of the pores, the effective diffusivities decrease sharply at low levels of deactivation and level off at the higher levels of deactivation. The results of the present study suggest that at low temperatures, when deactivation occurs by predominantly pore choking at low coke levels and by active site suppression at the higher coke levels, the effective diffusivity decreases very drastically at low coke levels and levels off at the higher coke levels (Fig. 8). Hence the physical model suggested in this work is consistent with Ref. *(20)*.

The physical model used in this work can also be related to the model proposed by Derouane *et al.* *(21)*. This model for sorption, diffusion and reaction is based on the van der Waals interactions between a reactant molecule and the curved external surface of the zeolite (near the pore mouth). Derouane *et al.* postulate the existence of a transport resistance, i.e., a surface barrier, for intracrystalline molecular diffusion, based on the argument that the transfer of the reactant molecule from the gas phase into the (restricted) zeolite pores is unlikely to occur by direct impingement, due to improper orientation of the reactant molecule. Therefore, the reactant molecule is initially adsorbed on the external surface of the zeolite, and this is followed by diffusion into the pores by "hopping" and "creep" motion. The reaction inside the pore takes place as the reactant molecule contacts an active site. Derouane *et al.* claim that the heat of adsorption rises rapidly when the size of the reactant molecule becomes comparable to the pore size of the zeolite, due to the surface curvature effects near the pore mouth. From this model, the heat of adsorption of *n*-hexane on a faujasite-type zeolite from the model is estimated to be 12 kcal/mol. This value is smaller than the heat of adsorption of cumene on REY zeolite used in this study. However, the critical diameter of cumene is 6.5 Å compared with 4.6 Å for *n*-hexane. Therefore, the heat of adsorption of cumene is expected to be higher than 12 kcal/mol due to the relative sizes of the two molecules and the curvature of the external surface of the zeolite near the pore mouth. This is consistent with the experimental value of 20 kcal/mol obtained in Ref. (*13*).

The model of Derouane *et al.* (*21*) matches the physical model used in this work and is also consistent with the models described earlier (*8–10*). All these models postulate the existence of a condensed phase on the external surface of the zeolite and the mechanism of condensation, diffusion and reaction in small-pore catalysts. The experimental results of this study are consistent with these models.

It is interesting to note that this model (*21*) predicts an increase in diffusivity with decreasing pore size. Physically, this would be because of an increased attraction as the pore walls approach the diffusing molecule. Such a trend could explain at least a portion of the increase in diffusivity with increasing coke levels seen in Figs. 8–10 assuming constant values of ΔH_{ads}.

The experimental results from this study can be compared with some work in the literature on deactivation mechanisms. Langner's work on cracking of propylene on $NaNH_4$–Y zeolite catalyst (*1*) indicates that the pore volume decreases in the beginning of the reaction and then remains nearly constant as the coke builds up on the catalyst at reaction temperatures below 300°C. However, at reaction temperatures above 300°C, the loss of pore volume is slower at the beginning of the reaction, but decreases continuously with coke formation until the pore volume is negligible. Relating these results to the mechanism of deactivation, Langner suggests that, at temperatures below 300°C, the coke precursors are formed on the active sites inside the pores, causing blockage of some pores. However, at temperatures higher than 300°C, coke molecules are macromolecular, graphite-like species that are formed at the exterior surface of the pore, leading to pore mouth blockage. The results of Langner are consistent with the physical model of the present work. Langner did not observe a change in deactivation mechanism at the low temperatures with increasing coke content on the catalyst, as suggested in this study. This may be due to the fact that Langner's work did not quantify the decrease in the active sites on the catalyst: his conclusions are based on the reaction conversions, coke levels and pore volumes as a function of time on stream. At the higher reaction temperatures, Langner's results are consistent with the results of this work, since he suggests that coke at these high temperatures is formed on the external surface of the zeolite until the pore mouth is blocked. Although this study does not discuss pore mouth blockage, it is to be noted that Langner's experiments were run for longer times on stream with significantly higher catalyst coke levels, up to 24%. Under such high coke levels, pore mouth blockage can be expected.

The work of Solinas et al. (*4*) on methylnaphthalene isomerization over Y zeolites at 360°C can be related to the results obtained in this study. From the relative rates of coking and reaction, Solinas *et al.* concluded that, at 360°C, coking primarily occurs by the suppression of active sites rather than by pore blocking. The results of the present study indicate that active site suppression is the predominant mechanism during deactivation at temperatures of 350°C and above for cumene cracking as well.

The results of Magnoux *et al.* (5a,b) indicate that choking of the pores can occur even at low coke levels. On HY zeolites, Magnoux *et al.* suggest that polyaromatic coke molecules are formed near the strongest Lewis and Brønsted acid sites. Such molecules affect the circulation of the reactant and products within the zeolite pores. At coke levels of 1%, the large polyaromatic coke molecules block the pores completely, preventing reactant access to the active sites. However, the smaller coke molecules limit the access of the reactant molecules to the acid sites but do not block the pores completely. The relative numbers of large and small coke molecules formed depends upon the size of the reactant and the zeolite pores. These results are similar to the results of this work since evidence of pore choking is seen at low coke levels.

The results of the present study can also be compared with the work of Bulow *et al.* (*3*) with HZSM-5 zeolites at 500°C. During mesitylene cracking, coke formed on the catalyst is deposited on the external surface of the zeolite. Bulow *et al.* attribute this to the relative sizes of the mesitylene and the pores of HZSM-5 zeolite. The results are consistent with the physical model of the present work. Since the relative sizes of mesitylene and cumene molecules are comparable, similar modes of deactivation can be expected during coking of the zeolite catalysts.

SUMMARY AND CONCLUSIONS

In this study, the Constant-Coke Arrhenius Plots (CCAP) was used to evaluate the mechanisms of catalyst deactivation by coking during cumene cracking over REY zeolites. The intrinsic rate constants and effective diffusivities were evaluated under actual reaction conditions, from the (experimentally-obtained) observed rate constants at different catalyst deactivation levels and different temperatures. The relative magnitudes of the changes in the intrinsic rate constants and effective diffusivities, with respect to the fresh catalyst, were related to the relative importance of active site suppression and pore choking. Thus the predominant mechanism of deactivation of catalysts was determined as a function of the level of deactivation of the catalyst and the reaction temperature.

The novelty of this approach is that the predominant mechanism of deactivation can be determined under actual reaction conditions, without using techniques that alter the catalyst structure (for example, crushing the catalyst) and techniques that use probe molecules at cryogenic conditions. By using an experimental value for the heat of adsorption of cumene on zeolite, the actual values of intrinsic rate constants and effective diffusivities for cumene cracking can be obtained at all temperatures and coke levels. The relative magnitudes of site suppression and pore choking can be obtained without knowledge of the heat of adsorption and its variation with coke level.

At the lower temperatures, the results indicate that at low coke levels, pore choking is the predominant mechanism of deactivation. However, at the higher coke levels, active site suppression becomes more significant. This can be explained in terms of the reaction of the reactant molecules in the zeolite pores. At the lower temperatures, the reaction occurs primarily inside the pores. Initially, coke forms inside the pores, thereby choking the pores. However, at higher coke levels (greater than two percent), active site suppression becomes significant as coke precursors deposit on the active sites. Further, at the higher coke levels, the reactions may occur to an increasing extent on the external catalyst surface, since it is more difficult for the reactant molecules to diffuse into the choked pores. In any case, suppression of the surface sites becomes significant at coke levels greater than 2%.

At the higher temperatures, the results indicate that suppression of the active sites is the predominant mechanism at all coke levels (up to 4%). This can be explained in terms of reaction occurring on the external surface of the zeolite. At higher temperatures, since the intrinsic rate of the reaction is very high compared to the rate of diffusion of the reactant into the pores of the zeolite, the overall rate of the reaction is more strongly influenced by the diffusion of the reactant molecules into the pores. As a result of the slow diffusion process, the reactant molecules react very rapidly on the catalyst surface, even before the molecules can diffuse into the pores. Therefore, the reaction occurs primarily on the active sites located on the surface of the zeolite rather than inside the pores.

The mechanisms of deactivation during cracking of cumene on REY catalysts compare very well with the theoretical and experimental work in the literature. However, due to the complex nature of the mechanisms of coke formation, the nature and characteristics of the coke and the mechanisms of cracking, it is important to note that the relative importance of active site suppression and pore choking mechanisms is depends strongly on the type of zeolite catalyst used, the reactant, and the temperature of the cracking reaction amongst other factors.

APPENDIX: NOMENCLATURE

A_H	Value of the high-temperature asymptote (lit/gm/s)
A_L	Value of the low-temperature asymptote (lit/gm/s)
C	Weight percent coke on the catalyst (%)
D_{eff}	Effective diffusivity of the reactant (cm^2/s)
E_d	Activation energy for diffusion (kcal/mol)
E_{int}	Activation energy for the reaction (kcal/mol)
E_{obs}	Observed activation energy for the reaction (kcal/mol)
f	Fraction contacting TGA sample pan
ΔH_{ads}	Enthalpy change of adsorption; negative of heat of adsorption (kcal/mol)
K_{ads}	Adsorption equilibrium constant (cm^3/gm)
k_{int}	Intrinsic reaction rate constant (cm^3/gm/s)
k_{obs}	Observed reaction rate constant (cm^3/gm/s)
l	Characteristic length parameter of catalyst particle, volume/external surface area (cm)
m_H	Slope of the high-temperature asymptote (K)
m_L	Slope of the low-temperature asymptote (K)
T	Temperature (K)
T_x	Temperature at the intersection of the high- and low-temperature asymptotes (K)
ρ	Bulk density of the catalyst (gm/cm^3)

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