

Constant-Coke Arrhenius Plots: A Diagnostic Tool

The presence of coke, highly unsaturated hydrocarbons produced by unneeded side reactions and strongly adsorbed on the catalyst, is known to decrease the activity of the catalyst. However the role of coke in the deactivation is not straightforward. If the coke molecule is adsorbed on a site hitherto active in the desired reaction, the catalyst loses activity because the site has been taken out of circulation. This is termed deactivation by direct site suppression. Phenomenologically, the intrinsic rate constant (on a total catalyst volume basis, for example) is decreased. On the other hand, the presence of coke molecules adsorbed on pore walls increases the resistance to mass transfer inside the catalyst pellet, decreases the concentration of reactant in the fluid phase above an active site, and thereby decreases the rate of reaction. This is termed deactivation by pore choking. Phenomenologically the effective diffusivity of the reactant inside the catalyst pellet decreases.

The two effects are not mutually exclusive; both or neither could be significant under appropriate conditions. Some data on deactivating catalysts show a rapid initial loss of activity followed by a slow and persistent decrease. The initially rapid drop could be interpreted as being caused by direct site suppression, since only a single coke molecule would be sufficient to tie up a single active site. The slow decrease could be caused by a monotonically increasing choking of the pore.

It is important to know which phenomenon is the predominant one in causing deactivation by coking. If both are important as suggested above, it is important to know the time on stream and/or coke level at which the transition may be considered to

occur. This is because changes in catalyst preparation required to minimize direct site suppression may be very different from those required to minimize pore choking. It is even possible that what decreases one effect may increase the other, so changes that are successful under one set of feed, catalyst, and reaction conditions may be spectacularly unsuccessful under another set of conditions.

Assignment of one or the other phenomenon to deactivation by coking requires the separate evaluation of the intrinsic kinetics and the effective diffusivity at the reaction temperature, pressure, and fluid phase composition as a function of coke level on the catalyst. Then a decrease in the intrinsic rate constant with increasing coke level might imply direct site suppression, while pore choking may be inferred if the effective diffusivity decreased with coke level. Needless to say the rate constant evaluated must be that of the actual reaction, since active sites may differ for different reactions. Similarly the effective diffusivity must be that of the reactant, since pore interactions with small probe molecules may be significantly less important than with large complex molecules. In general, however, the rate constant and effective diffusivity are coupled through the effectiveness factor and the Thiele modulus. Hence isothermal activity data, such as conversions at various times on stream or coke levels, do not yield the information required.

This work shows how modification of a technique recently reported by Wan (1) can be used to evaluate separately (pseudo-) first-order intrinsic rate constants and effective diffusivities of the reactant under actual reaction conditions. Using the original technique, Wan was able to estimate

effective diffusion coefficients of aromatic and naphthenic compounds over an uncoked zeolite catalyst while the cracking reaction was in progress. Repeating this for various types of zeolites, he was able to relate the effective diffusivity to the critical molecular size of the window aperture of the zeolite. We show below that a great deal more information can be extracted with a proportionately smaller increase in effort. The outcome here is primarily a recipe for qualitative assignment of pore choking and/or direct site suppression to any given deactivation by coke. More detailed quantitative results for a specific case will be published later.

The modified technique is as under. First-order (observed) rate constants for the overall reaction (k_{obs}) and the percentage of coke on the catalysts (C) are obtained for various times on stream in an isothermal reactor, and the experiment is repeated at several temperatures (T). The $k_{\text{obs}}-C-T$ data are recast into a set of Arrhenius plots ($\ln k_{\text{obs}}$ vs $1/T$), each plotted at a different but constant value of C . Then the work of Aris (2) and others predicts that two asymptotic straight lines can be drawn through the data, at sufficiently high and sufficiently low temperatures in turn. Two such sets of straight lines are shown in Fig. 1. At temperatures low enough that the

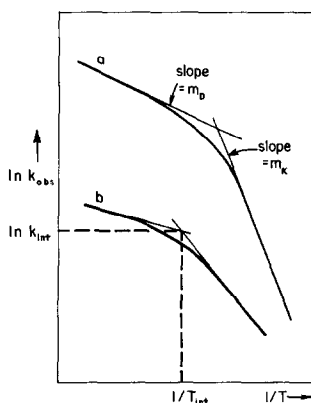


FIG. 1. Arrhenius plots at two different levels of coke on the catalyst. The coke level increases from curve a to curve b.

overall reaction in the largest catalyst particles is governed by intrinsic kinetics on the catalytically active sites, the observed rate constant can be set equal to the kinetic constant, k_K , assumed first order, i.e.

$$k_{\text{obsd}} = k_K. \quad (1)$$

At temperatures high enough that the overall reaction in the smallest catalyst particles is governed by diffusion through the pores and intrinsic kinetics

$$k_{\text{obsd}} = k_K/\phi. \quad (2)$$

Here ϕ is the generalized Thiele modulus for the collection of particles

$$\phi = \bar{l}(k_K/D_e)^{1/2} \quad (3a)$$

where \bar{l} can be considered as an average particle dimension

$$\bar{l} = \int l^3 n_l dl / \int l^2 n_l dl \quad (3b)$$

and D_e is the effective diffusivity of the reactant in the catalyst pore. In Eq. (3b) the limits of integration are from 0 to ∞ , and $n_l \Delta l$ is the number of particles of size between l and $l + \Delta l$. Equations (3) are derived by adding contributions to the total reaction rate from particles of all sizes.

For a given coke level, extrapolating the asymptotic straight lines corresponding to Eqs. (1) and (2) results in their intersection at a point (k_{int} , T_{int}) as shown in Fig. 1. At T_{int} , the right-hand sides of Eqs. (1) and (2) must be equal to each other and to k_{int} . This yields values of k_K and D_e at a particular temperature (T_{int}) and for the given coke level as

$$k_K(T_{\text{int}}) = k_{\text{int}} \quad (4a)$$

$$D_e(T_{\text{int}}) = (\bar{l})^2 k_{\text{int}}. \quad (4b)$$

The temperature dependence of k_K and D_e can be obtained by noting that the slopes of the low-temperature and high-temperature asymptotes, m_K and m_D , respectively, are related to the activation energies E_K and E_D of the rate constant and diffusion coefficient, respectively, via

$$m_K = -E_K/R \quad (5a)$$

and

$$m_D = -(E_K + E_D)/2R. \quad (5b)$$

In terms of the parameters k_{int} , T_{int} , m_K , and m_D , the intrinsic rate constant and effective diffusivity can be written

$$k_K(T, C) = k_{int}(C) \exp\left[-\frac{m_K(C)}{T_{int}(C)}\right] \exp\left[\frac{m_K(C)}{T}\right] \quad (6a)$$

$D_e(T, C)$

$$= (\bar{l})^2 k_{int}(C) \exp\left[\frac{m_K(C) - 2m_D(C)}{T_{int}(C)}\right] \exp\left[-\frac{m_K(C) - 2m_D(C)}{T}\right]. \quad (6b)$$

If this is repeated for a series of coke levels, only two of which are shown in Fig. 1, the variations (if any) in k_K and D_e with the level of coking can be ascertained. The relative magnitudes of these changes can be used to indicate the relative importance of direct site suppression and pore choking as the causes of the deactivation. If the deactivation is governed by one effect upto a certain coke level and the other effect at greater coke levels, as suggested earlier,

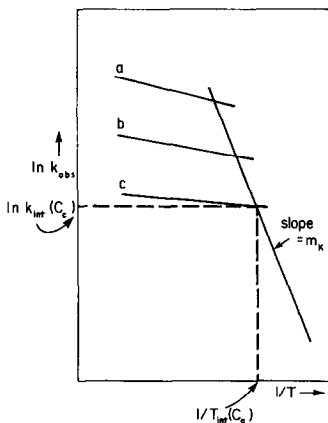


FIG. 2. Constant coke Arrhenius plots expected when deactivation is by pore choking only. The rate constant is independent of coke level and the diffusion coefficient decreases with increasing coke. All intersection points fall on a line of slope m_K , i.e., on the low-temperature asymptote.

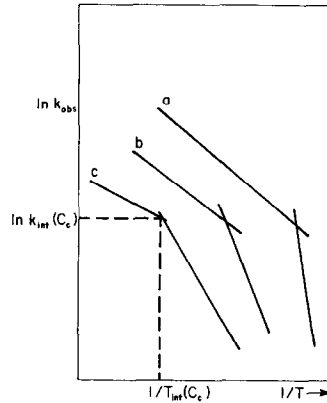


FIG. 3. Constant coke Arrhenius plots expected when deactivation is by direct site suppression only. The diffusion coefficient is independent of coke level and the rate constant decreases with increasing coke. All intersection points fall on an approximately horizontal line, i.e., the value of k_{int} is approximately independent of the coke level.

that too can be observed by this technique.

Criteria which determine if either k_K or D_e decreases with increasing coke level while the other is constant can be obtained as under. If k_K is independent of C while D_e is a function of C , i.e., if deactivation occurs by pore choking, then

$$\frac{d \ln k_{int}}{d(1/T_{int})} = m_K = \text{constant}. \quad (7)$$

In words, this implies that the low-temperature asymptote has a slope that is unchanged as the level of coke increased. Further, the locus of the intersection of the two asymptotes lies on the low-temperature asymptote. These criteria for deactivation by pore choking are illustrated in Fig. 2.

On the other hand, if D_e is independent of C while k_K decreases with increasing C , i.e., if deactivation is by direct site suppression, then

$$\frac{d \ln k_{int}}{d(1/T_{int})} = 2m_D - m_K = \text{constant}. \quad (8)$$

The term $(m_K - 2m_D)$ is of course the activation energy for diffusion, E_D/RT , which is normally a small number. Hence the locus of the intersection of the two asymptotes is

an approximately horizontal line. These criteria for deactivation by direct site suppression are illustrated in Fig. 3.

Data of $k_{obs}-C-T$ are difficult to come by in the literature. Two examples are given in Figs. 4 and 5. Interestingly, neither of them has the qualitative form of Figs. 1-3.

Figure 4, from the data of Ozawa and Bischoff (3), represents a situation where the adsorption enthalpy overshadows the intrinsic activation energy of the reaction, leading to observed reaction rates decreasing with temperature. Here the reaction controls the process at higher temperatures. Aside from that, the treatment of the data is unchanged. Since there are only three data points for each coke level, any asymptotes drawn must be viewed with extreme caution. However the lines drawn in Fig. 4 would appear to meet the criteria of Eq. (8) rather than those of Eq. (7). In other words the deactivation in this case is probably due to direct site suppression. This is not inconsistent with the conclusions reached by Ozawa and Bischoff.

Figure 5 is taken from the data of Langner (4). At sufficiently low temperatures, the observed rate constant decreases with temperature, but this is followed at higher temperatures by a dramatic reversal of the trend. Only a second reaction or set of reactions in parallel with the first can ex-

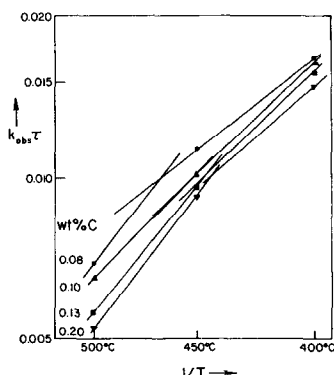


FIG. 4. Data of Ozawa and Bischoff (3). The positive slopes of all lines indicate strongly exothermic adsorption. Note that the k_{int} values as drawn are independent of the level of coke.

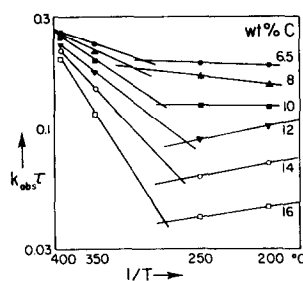


FIG. 5. Data of Langner (4). The increasing slopes of the low-temperature asymptote lines with increasing coke indicate adsorption-controlled reactions. The high-temperature asymptotes indicate the presence of parallel reaction(s). The vee-shaped nature of the asymptotes is not observed when the data are plotted at constant times.

plain this effect. Since the transition temperature is around 280°C, the parallel reactions are probably not those of the homogeneous uncatalyzed gas phase. Further the activation energy of the parallel set increases with coke level, not what is expected for a homogeneous reaction.

The following conclusions may be arrived at. For "conventional" relations between the observed reaction rate and temperature, the constant coke Arrhenius plot technique allows us to determine whether deactivation by coking occurs via the direct suppression of active sites or by choking of the pores. If both effects are observed, this technique would ascertain the conditions under which one or the other effect predominates.

"Unconventional" relations show up dramatically with this approach, as demonstrated by Figs. 4 and 5. In these cases, the use of this technique may be able to shed some light on the mechanism of the reaction and its dependence on the coking level.

It should be noted that if the data of Fig. 5 were recast as Arrhenius plots at constant time (not shown) rather than constant coke level, the Vee-shaped curve would not be observed. This emphasizes the diagnostic usefulness of this technique even (or especially) in cases when the mode of deactivation cannot be obtained from them in a straightforward manner.

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