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NOTES

Site-Localized Diffusional Effects

When a reaction within the porous structure of a catalyst is limited by mass transfer effects, the interior surface of the catalyst is exposed to a lower reactant concentration than occurs in the bulk gas phase. Hence, the rate of reaction is reduced and the basic kinetic character of the surface reaction (activation energy, reaction order, selectivity, etc.) is altered (*1*, *2*). These diffusion problems are generally treated on a macroscopic, or pellet basis, where concentration gradients are expressed as a function of location within the catalyst pellet. Little, if any, mention is made of the possible existence of concentration gradients in the immediate vicinity of very active sites. It is the purpose of this note to discuss the possible existence of such site-localized diffusional effects and to speculate on how these effects may alter the behavioral characteristics of catalysts.

Starting with a first-order, irreversible reaction

$$A \xrightarrow{k_s} B,$$

which is pore-diffusion limited, the reaction rate is

$$r = k_s(A_g)\bar{\eta} \qquad (1)$$

where $\bar{\eta}$ is the effectiveness factor, (A_g) is the bulk gas-phase concentration of A, and k_s is the intrinsic rate constant for the reaction. The $\bar{\eta}$ in Eq. (1) is considered to be an average value for the entire catalyst pellet. Classically, η is a function of the distance from the external pellet surface, varying from perhaps near unity at the pellet surface to near zero at the pellet center. The reason a pore-diffusion limitation occurs is that reactant cannot be transported to the surface fast enough to keep pace with a fast surface reaction.

The intrinsic activity of a catalyst is a function of an intensive factor, the activity per site, and an extensive factor, the total number of sites within a given catalyst pellet (i.e., active site density). Thus, for a homogeneous surface

$$k_s = kn_t, \qquad (2)$$

where k is the rate constant per site and n_t is the total number of active sites in the pellet. In a recent review article on site densities, it was estimated that 20–40% of modern catalytic systems have site densities of 10^{11} cm^{-2} or less with many site densities of 10^{9} cm^{-2} or less (*3*). A low site density means that only a very small fraction of the catalyst surface is active and that these active sites may be several hundred or even several thousand angstroms apart on the catalytic surface. At any given k_s value, an infinite number of values of k or n_t are possible as shown in Fig. 1a. Since n_t or k can theoretically have almost any value, it is interesting to speculate on the catalytic behavior which various combinations might produce within a catalyst pellet. There are four combinations of extremes which can occur:

low k–small n_t
low k–large n_t
high k–large n_t
high k–small n_t

with, of course, an infinite number of intermediate values and combinations being possible.

The *low k–small n_t* case would coincide with widely separated sites of low activity.

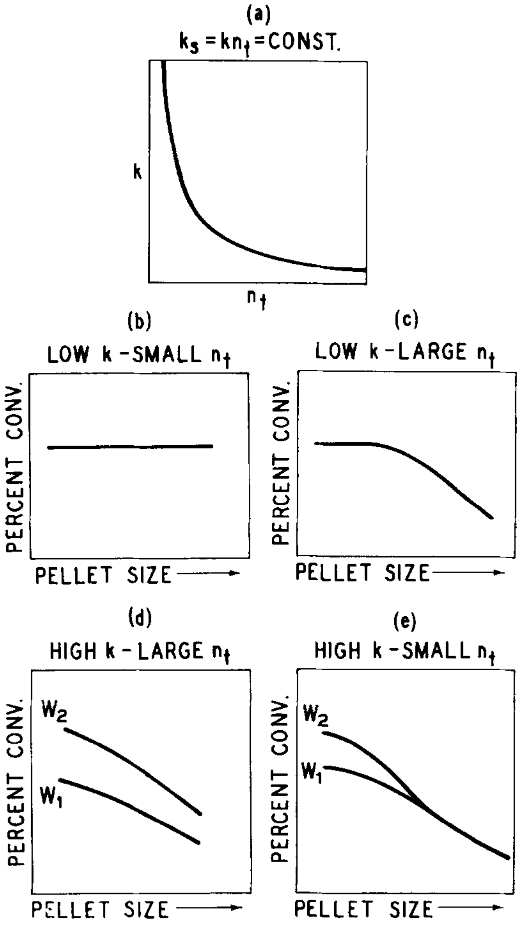

FIG. 1. The effects of k and n_t on catalyst behavior.

Conversion would be low and no pore-diffusion limitation would be expected as shown in Fig. 1b.

The *low k–large* n_t case is one where a large number of low activity sites are reasonably close together on the catalyst surface. This case may be the one most frequently encountered in heterogeneous catalysis. If the reaction is pore-diffusion limited, a reduction in pellet size at constant space velocity should cause $\bar{\eta} \rightarrow 1$ and, hence, constant activity per unit weight of catalyst should be obtained as shown in Fig. 1c.

In the *high k–large* n_t case, each catalyst pellet will contain a large number of very active sites. The catalyst is so active that the reaction is limited by both pore and interphase diffusion. In fact, most of the reaction likely occurs in the outside shell of the catalyst pellet. Thus, when two different weights of catalyst are compared at constant space velocity as a function of pellet size, behavior similar to that shown in Fig. 1d is expected.

In the *high k–small* n_t case, these very active but widely separated sites may be limited by site localized effects. In other words, each site may be so active that the reactant cannot diffuse to the site location fast enough to keep pace with the reaction, and a concentration gradient is developed in the vicinity of each of these very active centers. In addition to this localized limitation, there may be some accumulative limitative caused by localized concentration gradient overlap, unless the sites are sufficiently far apart. This behavior can be described for sites of equal intrinsic activity by an equation of the type:

$$r = k\Sigma(n_i\eta_i)A_g \approx kn_t(A_g)\bar{\eta}, \qquad (3)$$

where the sites effectiveness factor, η_i, is a function of k and site environment. If an average $\bar{\eta}_i$ is used as shown above, Eq. (3) is similar in form to Eq. (1) which describes the classical pore diffusion case, except that decreasing n_t at constant k for these very active sites will not cause $\bar{\eta}_i \rightarrow 1$, as in the low k–large n_t case. Thus, it is possible to have low experimental reaction rates which are limited by site localized diffusional effects.

The behavior of these very active, widely separated sites within porous catalyst crystallites or pellets should have interesting kinetic characteristics. Since most of the surface area of a porous catalyst is found within the microporous structure of the support, most of these very active sites should be located in micropores (assuming uniform promoter distribution). If n_t is small, some micropores could contain active sites, while most others have none. Concentration gradients will then develop in these active pores but not in the inactive pores. The development of concentration gradients in the pellet's macroporous structure would then depend on the number of active micropores which feed it. It should be possible to have micropore-diffusion limitation both with and without limitations occurring in the macroporous structure of the pellet.

In large catalyst pellets, most of these active pores will open into macropores, or into the large interstitial spaces, which surround the small crystallites or particles from which the pellet is constructed. When most of these active pores open internally, little, if any, interphase-diffusion limitation should be observed. If, however, most of the "active sites" were located on the external surface of the pellet, or in pores which open on or near the external surface, then one might find experimental evidence for interphase-diffusion limitation. As pellet size is reduced, a larger and larger percentage of these active sites or active pores will be located at or near the particle's external surface. Hence, a reduction in catalyst pellet size for the high k–low n_t case should enhance the possibility for observing interphase mass-transfer limitations perhaps even as shown in Fig. 1e for two different weights of catalyst at constant space velocity. Hence, it seems possible to have interphase-diffusion limitations occurring at low reaction rates or at low levels of conversion in spite of classical calculations to the contrary.

Consider, for example, the idealized behavior of a dead end, cylindrical pore, 50 Å radius, which opens on the external surface of a large spherical pellet and contains one very active center or site. For an irreversible, first-order reaction in this active pore, one can equate the rates of mass transfer of reactant to the pore mouth and Knudsen diffusion in the pore to the surface reaction rate as follows:

$$r = k_c a c_t (y - y_{pm}) = \{[D_k a c_t (y_{pm} - y_s)]/x_o\} = k_s c_t y_s. \quad (4)$$

By eliminating pore mouth and site reactant mole fractions (y_{pm} and y_s), Eq. (4) reduces to

$$r = \frac{k_c a c_t y}{[1 + (k_c x_o/D_k) + (k_c a/k_s)]}, \quad (5)$$

where k_c and D_k are the appropriate diffusion coefficients, a is the pore mouth area, c_t is the total gas-phase concentration, k_s is the intrinsic surface rate constant, y is the gas-phase mole fraction of reactant and x_o is the thickness of the Knudsen diffusion layer (or the distance from the active center to the pore mouth). When $k_s \gg k_c\, a$, Eq. (5) reduces to

$$r = \frac{k_c a c_t y}{[1 + (k_c x_o/D_k)]}, \quad (6)$$

which suggests some interesting possibilities. If, for example, the active center were located at or near the pore mouth where $x_o \to 0$, then the rate of reaction would be limited by interphase-diffusion effects. When the active center is located a long distance from the pore mouth (i.e., x_o is large), Eq. (6) predicts that the rate will be limited by pore-diffusional effects. Hence, depending on the value of x_o, the reaction rate in this active pore could be limited by either or both diffusional effects.

A numerical example of the behavior of this active pore as a function of x_o and particle Reynolds number is shown in Fig. 2. The low Reynolds number correlation of Petronic and Thodos (*4*) was used to evaluate k_c ($N_{Sc} = 1$, $N_{Re} = 5$ and 10), while D_k was calculated as shown by Satterfield (*1*). A gaseous reactant of 42 mol wt presumably was passed through a packed bed of 1 cm diam spherical pellets at 400°C and 1 atm pressure. Even for this simple model, if the active pore is limited by the site localized, Knudsen pore diffusion, a decrease in pellet size will cause x_o to decrease, and the reaction to become limited by interphase-diffusional effects. Perhaps the most unusual thing about Fig. 2 is the magnitude of x_o, where the transition from interphase to pore limitation occurs. These active centers could be buried as much as 10^6 Å (0.01 cm) below the external surface, and yet create a concentration gradient which extends into the bulk gas phase.

The behavior of this simple model may be rather far removed from the behavior of a real catalyst. However, interphase-diffusion limitations have been observed for the disproportionation of propylene on WO_3–silica catalysts at reaction rates sev-

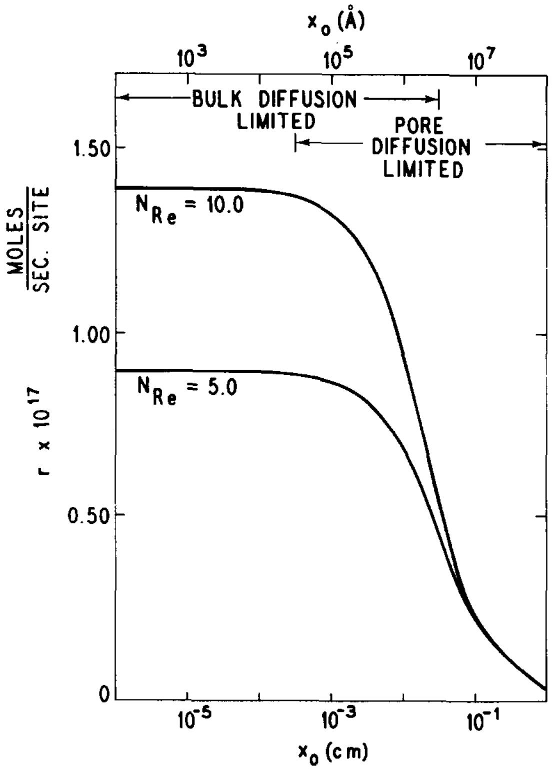

FIG. 2. Activity in one active pore as a function of x_0 and N_{Re}.

eral orders of magnitude lower (10^2–10^4) than where such limitation should occur, according to classical calculations (*5*). A site localized diffusional limitation at very active, but widely separated sites, was used to explain these unusual results.

It is concluded that perhaps more attention should be given to the possible existence of site-localized diffusional effects. This is particularly important since active site densities may be several orders of magnitude less than usually supposed (*3*) and, hence, site activities may be several orders of magnitude higher than usually supposed. Site-localized diffusion limitations may occur even at low bulk reaction rates where classical calculations predict no limitation. Perhaps diffusional effects should be excluded on the basis of experimentation rather than calculation, and even then the possibility of a surface reaction being limited by site-localized diffusion should be considered.

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A. J. MOFFAT

Phillips Petroleum Company
Research & Development Department
Bartlesville, OK 74004

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Catalytic Oxidation of Olefins over Metallic Palladium Suspended in Water

Since the development of the Wacker process, catalytic reactions of olefins using palladium salts have been studied by many workers (*1*). However, little is known about the catalytic activity of palladium metal in the selective oxidation of olefins. Patterson and Kemball (*2*) reported that the main reaction in the catalytic oxidation of olefins over palladium film was complete oxidation, but that small amounts of acetone were produced in the oxidation of propylene and higher olefins. The authors