ACKNOWLEDGMENTS

The authors wish to express their appreciation to G. W. Schwert and S. K. Chen for helpful discussions and P. C. Yang for analysis of the α-chymotrypsin. This work was supported under AEC contract AT(40-1)-3913 with David M. Richman as Project Manager.

NOTATION

b = dimensionless equilibrium parameter
C_2 = fraction of bottom reservoir dead volume to displacement, dimensionless
C_f = trypsin concentration in fluid phase, mg/ml
C_s = trypsin concentration on solid phase, mg/ml CHOM-Sepharose
h = packed height of column, mm
K = equilibrium constant, ml solution/ml CHOM-Sepharose
L_1, L_2 = penetration distance of concentration front, mm
m = equilibrium constant parameter defined by Equation (7), dimensionless
n = number of cycles
y_B = concentration of trypsin in bottom syringe, mg/ml
y_0 = initial concentration of trypsin in column, mg/ml
y_0' = initial concentration of trypsin measured, mg/ml

Greek Letters

α = slope of line given by Equation (2)
ϵ = column void fraction

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Manuscript received August 13, 1973; revision received March 18 and accepted March 19, 1975.

Catalytic Activity and Selectivity on Heterogeneous Surfaces with Mass Transfer

Effective reaction rates and selectivities on surfaces having active and inactive regions are calculated for systems in which diffusion of reactants and products through a boundary layer is significant. With a single reaction it is shown that rates are larger than those calculated assuming area weighted averages. The selectivity of production of an intermediate in a series of reactions on a heterogeneous surface is higher than on a homogeneous surface, and with parallel reactions selectivities may be lower or higher depending on the kinetics of the competing reaction.

Numerical examples from NH_3 oxidation on a Pt gauze and CO oxidation in the automotive converter indicate that these effects may be important in determining selectivities and conversions in some industrial reactors.

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SCOPE

Catalytic reactions on external surfaces have been studied theoretically by many investigators over the past two decades. Chung (1965) reviewed the literature in this field stressing the coupling of boundary layer and finite reaction rate. Since that time several additional papers have been published (Lindberg and Schmitz, 1969; Shirotsuka and Saro, 1969; Mihail, 1972). All these investigators have considered a uniformly active solid surface in contact with a gas. However, it is well known that most adsorbent surfaces exhibit heterogeneity with respect to their interactions with adsorbing gases. A recent paper by Rudzinski (1974) reviews this topic briefly, but to our

knowledge the coupling between mass transfer and surface heterogeneities has not been examined theoretically. Moffat, Clark, and Johnson (1970, 1971) observed rates of olefin disproportionation on supported WO_3 which were much higher than could be accounted for by mass transfer to an uniform surface, and they assumed that reaction was occurring on small, widely separated active sites.

Surface heterogeneities must be accounted for in any quantitative descriptions of catalytic reaction rates in terms of adsorption, desorption, and reaction parameters. While the effective rate expressions on heterogeneous surfaces can be easily written down in terms of these paramters on patches of specified areas, in all practical situations kinetics can be thoroughly disguised by mass transfer effects which frequently accompany industrial catalytic reactions. This is especially important in fast oxidation reactions which occur on the external surfaces of low area catalysts.

In this paper we consider simple models incorporating both surface heterogeneities and external mass transfer to see how they affect overall catalytic reaction rates.

CONCLUSIONS AND SIGNIFICANCE

Surface heterogeneities can strongly affect the properties of catalysts beyond those associated with area averaging. For example, the effective reaction rate becomes insensitive to the fraction of the total area which is active and to the kinetics when mass transfer is important. Also, in multiple reaction systems the selectivity can be orders of magnitude different than that calculated from an area weighted average, and this can be either lower or higher depending on whether the reactions occur in series or parallel and whether individual rates occur on the same or different patches.

Many of the desirable and undesirable properties of particular catalysts may be associated with the arrangements of regions of particular geometries and the consequent mass transfer inhibition or enhancement of reactions leading to particular product species rather than with simple surface area alone. Certainly these effects should be investigated in more detail as more reliable data on catalyst geometry and structural anisotropies in reaction kinetics become available.

MATHEMATICAL MODELS

We shall develop several models of reactions on a surface containing regions of different reactivities. In all cases we assume a flat surface with regularly spaced stripes or circles of high activity with reactants diffusing from a homogeneous gas phase through a boundary layer specified only by a thickness δ and a boundary layer diffusivity $\mathcal{D}$. This is obviously a gross simplification of actual physical situations but should qualitatively correspond to mass transfer limited reactions on gauzes and foils as long as gas flows are highly turbulent and surface roughness is small compared to the boundary layer thickness.

We shall first consider the simple case of a completely diffusion limited reaction on a surface with stripes and circularly shaped active regions, then examine the case of a finite reaction rate, and next investigate selectivities for multiple reaction systems. Finally the calculations will be illustrated with numerical examples to show how these effects can influence reaction rates and selectivities under realistic catalytic reaction conditions.

We are interested in overall effective reaction rates per unit surface area for specified kinetics on individual patches. In the absence of mass transfer, this would be

$$\bar{r}_{max} = \frac{\Sigma A_n r_n}{\Sigma A_n} \tag{1}$$

With mass transfer this is expressed as a comparison between actual rate and the maximum rate described through an effectiveness factor, or in multiple reactions by the selectivity of production of particular products. To evaluate these quantities, we need concentrations and their derivatives as a function of position in the boundary.

Consider a system consisting of active stripes of width $2l$ and a length much greater than $2l$, which are evenly distributed on an otherwise inert surface, (Figure 1) covered by a stagnant gas film of thickness δ in which the diffusivity of species A is $\mathcal{D}$. Beyond the film the gas is well mixed. Reactant diffuses through the film to the surface and reacts on the active stripes. A steady state mass balance on the species A yields

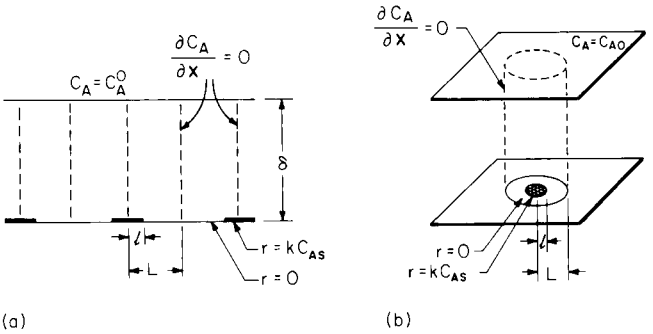

Fig. 1. Sketch of systems and parameters used for calculations of effective rates and selectivities.

$$\nabla^2 C_A = \frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} = 0 \tag{2}$$

with boundary conditions

$$\frac{\partial C_A}{\partial x} = 0\ , \quad x = 0 \quad \text{and} \quad x = L \tag{3a}$$

$$\frac{\partial C_A}{\partial y} = 0\ , \quad y = 0 \quad \text{and} \quad l < x < L \tag{3b}$$

$$\frac{\partial C_A}{\partial y} = \frac{r_A}{\mathcal{D}}, \quad y = 0 \quad \text{and} \quad x < l \tag{3c}$$

and

$$C_A = C_A^0\ , \quad y = \delta \quad \text{all} \quad x \tag{3d}$$

Concentration profiles were obtained numerically by solving Equations (2) and (3) by a finite-difference approximation using either 20×20 or 40×40 matrices. In some cases a variable grid size was used in order to provide a higher density of grid points around the discontinuity at $x = l$. Concentrations and rates are believed to be accurate within a few percent in all calculations.

MASS TRANSFER CONTROL

In this section we consider rates of reaction on active stripe and circular patches for the situation where mass

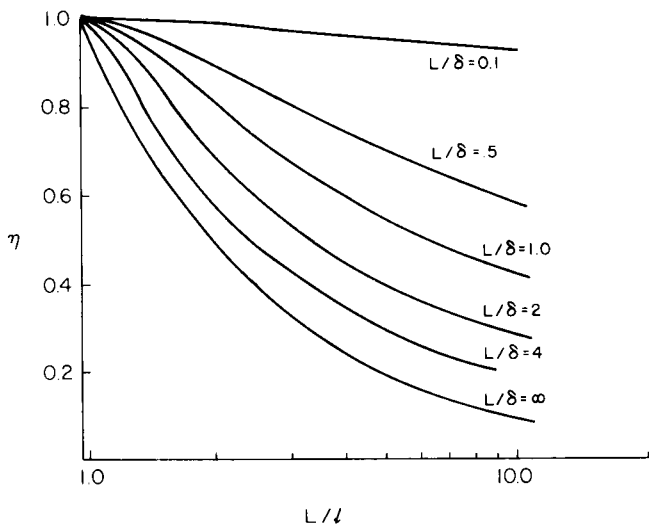

Fig. 2. Effectiveness factor for a diffusion limited reaction, Equation (5), vs. the ratio of total to active area L/l on a flat surface consisting of active stripes of width $2l$ separated by a distance $2L$. When the boundary layer thickness δ is much greater than l, the rate is that of an uniformly active surface while $\eta \sim l/L$ as $L/\delta \rightarrow \infty$.

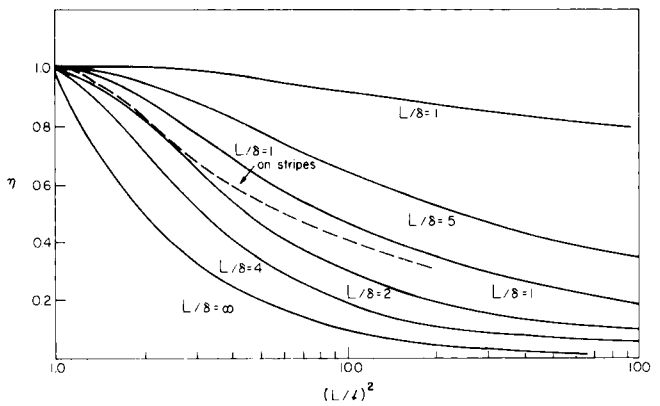

Fig. 3. Effectiveness factor for a diffusion limited reaction, Equation (5), vs. the ratio of total to active area L/l^2 on a flat surface consisting of active circular regions of radius l separated by a distance $2L$. The dashed line shows the corresponding curve for striped active regions, Figure 1, for $L/\delta = 1$.

transfer is much slower than the surface reaction rate. In this case C_A is very small over the active region, and the boundary condition of Equation (3c) becomes $C_A(y = 0, 0 < x < l) = 0$. The effective rate is calculated from the equation

$$r = \frac{\mathcal{D}}{L} \int_0^L \left(\frac{\partial C_A}{\partial y}\right)_{y=\delta} dx \qquad (4)$$

and we define an effectiveness factor as the ratio of this rate to the rate on a uniformly active surface:

$$\eta = \frac{\delta}{LC_A{}^0} \int_0^L \left(\frac{\partial C_A}{\partial y}\right)_{y=\delta} dx \qquad (5)$$

Figure 2 shows a plot of η vs. L/l for a range of values of L/δ. If the width of the active areas is much larger than the boundary layer thickness, $L/\delta = \infty$, then $\eta \simeq l/L$ and when the boundary layer is very thick, $\eta \rightarrow 1$. The latter case gives the expected result that the entire surface appears active even though the fraction of the actual active area is less than 0.1 of the total.

The results for the case of circular active regions are shown in Figure 3. The abscissa in this figure is $(L/l)^2$ since this is the ratio of total to active areas. As before, $\eta \simeq (l/L)^2$ as $L/\delta \rightarrow \infty$ and $\eta = 1$ as $L/\delta \rightarrow 0$. The approximation of cylindrical symmetry around each patch obviously breaks down for $L/l \simeq 1$.

The effectiveness factors vs. ratio of total to active area for stripes and circular patches are identical in the limits of $L/\delta \rightarrow \infty$ and $L/\delta \rightarrow 0$. The dashed curve in Figure 3 shows η on stripes for $L/\delta = 1$, and this is very close to that on circular patches for $L/\delta = 1$. We conclude that mass transfer effects are not strongly sensitive to the exact shapes of the active regions, at least in this system. We shall carry out further calculations only for stripes, but by the above arguments these results should be approximately correct for any patch geometry.

FINITE REACTION RATES

In the previous example the rates were independent of the reaction kinetics because the reaction was mass transfer controlled. We next consider the situation for finite reaction rates on active stripes for first-order kinetics $r_{surface} = k\,C_{As}$. There are now three dimensionless parameters: the fraction of active surface l/L, the ratio of half the distance between stripes to the boundary layer thickness L/δ, and the ratio of reaction rate constant to mass transfer coefficients expressed as the Damkoehler number $Da = k\delta/D$.

Here we define an effectiveness factor as the ratio of the effective reaction rate to the rate on a uniformly active surface with no diffusion limitation. For a first-order irreversible reaction on stripes of half width l, this is

$$\eta = \frac{\int_0^l C_A(x, y = 0)\, dx}{L\, C_A{}^0} \qquad (6)$$

Figure 4 shows plots of the effectiveness factor defined above vs. $k\delta/\mathcal{D}$ for $l/L = 1.0$, 0.1, and 0.01. In the reaction limited situation, Da small, η approaches l/L. The reaction rate is now the area weighted average of Equation (1) and is independent of the dimensions of the active regions. For $Da > 20$, the diffusion controlled situa-

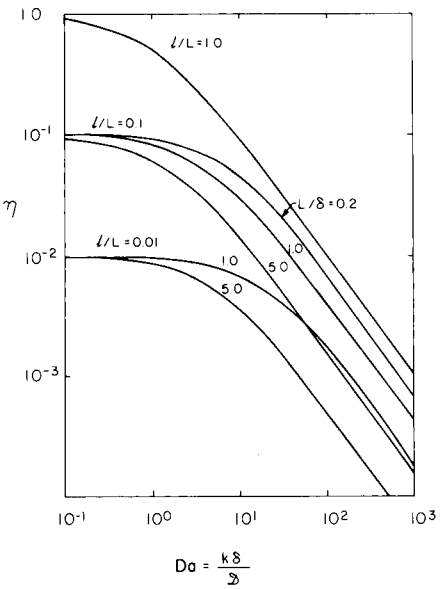

Fig. 4. Effectiveness factor defined by Equation (6) vs. $k\delta/\mathcal{D}$, the Damkoehler number, for indicated fractional active area l/L on a striped surface. For series reactions k in Da is the rate constant for the first reaction k_1.

tion, the η defined by Equation (5) and plotted in Figure 2 is also appropriate.

For the uniform surface $l/L = 1$, it is easy to show from Equation (6) that η is given by the expression

$$\eta = \frac{1}{1 + \frac{k\delta}{\mathcal{D}}} = \frac{1}{1 + Da} \tag{7}$$

SELECTIVITY

The selectivity of reactions in which a desired product species can react also depends on the ability of this species to escape from the catalyst surface. Consequently diffusion limitations will always lower the selectivity of production of intermediates below that obtained under the kinetically controlled conditions. This problem has been treated in detail for simple series reactions with external mass transfer limitations on a homogeneous flat surface and with pore diffusion (Kramers, 1962; Aris, 1975).

We shall first consider the selectivity to be expected on a striped surface for the series reactions

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

where A is supplied from the gas phase, A, B, and C have identical mass transfer coefficients, and the reactions are first order in C_A and C_B, respectively, on the active stripes of half width L. Outside of the boundary layer $C_A = C_A^0$ and $C_B = 0$, that is, the conversion is assumed to be sufficiently low that the system behaves as a differential reactor.

The selectivity is defined as

$$S = \frac{k_1 \int C_{As}\, dx - k_2 \int C_{Bs}\, dx}{k_1 \int C_{As}\, dx} = 1 - \frac{k_2}{k_1} \frac{\int C_{Bs}\, dx}{\int C_{As}\, dx} \tag{8}$$

where the integrals are over the active region on the surface. For a uniformly active surface with the above boundary conditions, it is easy to show that

$$S = \frac{1}{1 + \frac{k_2\delta}{\mathcal{D}}} \tag{9}$$

The selectivity does not depend on the rate constant of the first reaction k_1 because of the requirement that $C_B = 0$ above the boundary layer. The solid curve in Figure 5 is a plot of S vs. $k_2\delta/\mathcal{D}$, the Damkoehler number Da_2, for a homogeneous surface.

Figure 5 shows plots of selectivity vs. Da_2 for indicated values of l/δ with active areas l/L of 0.1 and 0.01. These were calculated by solving simultaneously the equations $\nabla^2 C_A = 0$ and $\nabla^2 C_B = 0$ with boundary conditions similar to Equation (3) and those discussed above.

Surface heterogeneity markedly increases the selectivity above that on the homogeneous surface. The selectivity is increased by a large factor above that predicted by Equation (9) and, more important, S can remain near unity for Damkoehler numbers large enough (Da_2 between 1 and 10) that S would have fallen to a low value if the surface were homogeneous.

The cause of increased selectivity of production of an intermediate in series reactions on a heterogeneous surface is easily interpreted. Intermediate B can more easily escape from the active surface on a patchy surface because it can diffuse laterally as well as normal to the surface while on a homogeneous surface only the latter occurs.

Concentration profiles of reactant A and intermediate B

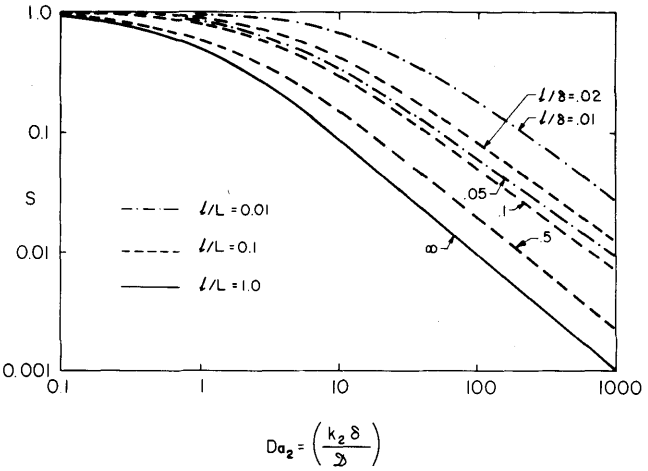

Fig. 5. Selectivity of production of B in the series reaction A→B→C vs. $k_2\delta/\mathcal{D}$ on a striped surface. For small l/L, the selectivity may remain nearly unity under conditions where S would be < 0.1 on a uniform surface.

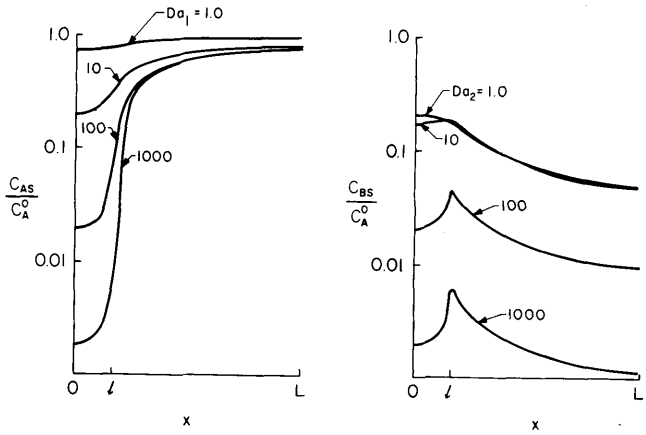

Fig. 6. Plot of concentrations of A and B near the surface for series reactions A→B→C with $k_1 = k_2$ vs. position x on the surface. C_{Bs} peaks near the edge of the active region because the rate at which it is being produced is largest there.

at the surface possess interesting features. Figure 6 shows C_{As} and C_{Bs} vs. position on the surface for indicated values of Da_1 and Da_2. (In this example $k_1 = k_2$ so that $Da_1 = Da_2$.) C_{As} increases rather sharply as one goes away from the active region as expected, but C_{Bs} exhibits a maximum for large Da_2. The rate of the first reaction is always highest on the edge of the active area because the concentration of reactant on the active area is a maximum there. For low Da_2 the intermediate B is removed rapidly from the surface, and the concentration of B is a maximum on the center of the active area. For high Da_2 the removal of B from the active area is less efficient. Consumption of B is higher in the center, and the concentration of B peaks near the edge of the active area. In other words, the concentration of B on the active surface is a maximum where the rate of production of B is a maximum.

For the parallel reactions

$$\begin{matrix} & k_1 & \\ A & \rightarrow & B \\ & k_2 & \\ A & \rightarrow & C \end{matrix}$$

the selectivity of production of B is exactly independent of active surface areas or dimensions as long as the rates depend only on C_{As}. If both rates are the same order in

C_{As}, the selectivity is also independent of mass transfer resistances. If the first reaction occurs on one region and the second on the other region, there is obviously a competition of the two regions for A. Consequently mass transfer limitations will enhance the selectivity for production of the species with the higher rate compared to the kinetically limited selectivity.

DISCUSSION

We have shown that both total reaction rates and selectivities of product distributions can be strongly altered in the presence of surface heterogeneities and mass transfer. We shall next comment on the validity and possible utility of the calculations and then show that these effects should be significant in two important industrial catalytic reactions: NH_3 oxidation on Pt gauzes and CO oxidation on supported Pt.

First, it should be noted that only rather fast catalytic reactions can exhibit external mass transfer. The fastest oxidation reactions should have Damkoehler numbers not much above 10 at one atmosphere, although since $\mathcal{D} \sim 1/P$, mass transfer becomes more important in very high pressure processes. Also, these calculations are only applicable to situations where surface structures are large compared to the gaseous mean free path because we have used continuum diffusion equations. The mean free path is 1000 Å at 1 atm and decreases with increasing pressure as $\sim 1/P$. Therefore, at high pressures these calculations should become more realistic.

Finally, we suggest that the many simplifying assumptions which we have used to develop workable models should not seriously impair the general validity of the results, although of course the calculations should have only qualitative significance when applied to any particular catalytic reaction system. The major parameters of interest are boundary layer thickness, mass transfer or molecular diffusion coefficients, size of heterogeneities, fraction of surface which is active, and reaction kinetics. These can only be estimated crudely for any real catalyst. Therefore it should be appropriate to assume that the results are roughly independent of the shape and distribution of various regions on the surface as long as these are much smaller than the boundary layer thickness. Obviously the model breaks down if the L is comparable to δ because δ is then not a well-defined quantity.

These calculations should be appropriate to surface heterogeneities caused by crystallographic anisotropies, by active regions associated with grain boundaries or lattice steps, and by supported metal crystallites on oxides and other chemically heterogeneous catalyst surfaces where external mass transfer limitations exist.

NH_3 Oxidation

This reaction is carried out industrially by passing 10% NH_3 in air over a thin layer of Pt-Rh gauze catalyst at ~ 900°C. All NH_3 is decomposed in a very short contact time (~ 1 m s) on the catalyst, and on an activated catalyst the conversion to NO is between 95 and 99%, the rest going to N_2. While this has been shown to be a series-parallel reaction (Pignet and Schmidt, 1974), in excess O_2 it can be approximated as a simple series process

$$NH_3 \rightarrow NO \rightarrow N_2$$

which is the reaction scheme of Figure 5. Microscopic examination (McCabe et al., 1974) shows that the gauze surface consists of flat facets between 2×10^{-4} cm and 5×10^{-4} cm in size. While data on single crystal planes are not yet available, indirect evidence suggests that reaction rates vary considerably between crystal planes. On the gauze converter we may estimate from Nowak (1966) $\delta \simeq 3 \times 10^{-3}$ cm, and laboratory kinetic data are available on the two reaction rates (Pignet and Schmidt, 1974). From these we estimate that in industrial reactors $Da_1 \approx 2.4$, $Da_2 \approx 0.8$, $L/\delta \approx 0.06$, and $l/L \approx 0.3$.

If the surface were homogeneous, Figure 5 gives a selectivity of $\simeq 0.6$ on a homogeneous surface, significantly lower than the 0.95 observed in practice. However, for the parameters given above on the heterogeneous surface Figure 5 gives $S > 0.9$.

CO Oxidation in Automotive Converters

CO is oxidized to CO_2 in a large excess of O_2 on ~ 1000 Å particles of Pt supported on Al_2O_3. While this is a porous support, the residence time is so short that efficient design requires that the Pt particles be on or near the external surface of the pellet or monolithic support. Consequently the active Pt clusters, comprising $\sim 5\%$ of the total external area, correspond approximately to active circular regions on a flat inert surface. From converter flow conditions, we estimate $\delta \simeq .04$ cm and kinetics of CO oxidation have been measured by Hori and Schmidt (1975). These parameters give $Da = 25$, $l/\delta \simeq 0.02$, and $l/L \simeq 0.05$, and the effectiveness factor this system is calculated from Figure 4 to be lower than that on a uniform surface by a factor of ~ 10.

However, Figure 4 shows that under these conditions the rate is only weakly dependent on l/L. This implies that the rate is almost independent of the amount of Pt in the catalyst if the number of particles and their spacing is fixed. Also, the rate of reaction may remain unchanged in the presence of poisons which only block part of the surface on each particle.

SUMMARY

These calculations show that the coupling between external mass transfer and surface heterogeneities can significantly alter catalytic reaction rates and selectivities from those predicted by considering either effect alone. The models we have developed are necessarily crude, but these figures should permit one to estimate behavior in a reaction system knowing only mass transfer coefficients, reaction rates on active regions, and dimensions of the surface structures. In fact, on any real catalyst one actually will have a distribution of activities on many patches of widely varying sizes. Therefore, more realistic calculations are not justified at present since the corresponding data are not available.

The calculations for NH_3 and CO oxidation indicate that the selectivity of the first reaction is significantly increased by surface heterogeneities and that the reactivity of the second depends strongly on the size and distribution of metal crystallites. These are to our knowledge the only reaction systems for which necessary information or kinetics and surface structure are available, but similar influences on reaction rates and selectivities should be expected for all fast catalytic reactions.

ACKNOWLEDGMENT

This work was partially supported by National Science Foundation Grant GK16241.

NOTATION

A_n = area of patch n in Equation (1)
C_A^0 = concentration of A outside the boundary layer
C_j = concentration of species j
C_{js} = concentration of j on the surface
Da_i = Damkoehler number for reaction i, Equation (7)
$\mathcal{D}$ = mass transfer coefficient
k_i = reaction rate constant for reaction i

l, L = length defined in Figure 1
x, y = coordinates
r = effective reaction rate, Equation (4)
r_n = reaction rate on patch n in Equation (1)
$\bar{r}_{max}$ = average effective reaction rate, Equation (1)
S = selectivity, Equation (8)

Greek Letters

δ = boundary layer thickness
η = effectiveness factor, Equations (5) and (6)

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Manuscript received January 17, 1975; revision received March 27 and accepted March 31, 1975.

Mechanics of Steady Spinning of a Viscoelastic Liquid

The equations for steady isothermal spinning of a viscoelastic liquid are solved for a fluid model with constant modulus and a single constant relaxation time. High stress levels are predicted for elastic liquids, and the velocity approaches a linear profile in the limit of maximum drawdown. These predictions are in accordance with the observed behavior of polymeric liquids in isothermal spinning. Relaxation times computed from spinning data of Spearot and Metzner and Acierno et al. for four low density polyethylene melts are comparable to those measured rheogoniometrically, though the spinning relaxation times are 20 to 80% larger.

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SCOPE

Spinning is the process of drawing a liquid into a filament or a sheet. The mechanics of steady spinning of low molecular weight Newtonian liquids is well understood, with good agreement between theory and experiment. The steady spinning of viscoelastic polymer melts and solutions, in contrast, is not well understood. There are major qualitative differences in the velocity and diameter profiles observed in the spinning of Newtonian and polymeric liquids. No analysis which can explain these differences has been published. Very high stresses are observed experimentally in the spinning of polymeric liquids relative to the stresses in a Newtonian liquid of the same viscosity under comparable processing conditions. These stresses cannot be predicted quantitatively, and the qualitative theoretical expectation of high stresses is usually founded on an a priori assumption of the kinematics in combination with an analogy to uniform transient stretching.

The industrial importance of spinning is only one reason for interest in the process. Spinning is an extensional flow field and it is usually a high Deborah number process; that is, large stress changes occur over a time scale which is comparable to the fluid relaxation time. In this sense, it is a prototype of many practical polymer processing situations, which tend to be high Deborah number processes with an important extensional component in the flow field. In contrast, nearly all analyses of the flow of polymeric liquids which have been successfully compared with experiments have been for shearing flows with no extensional component or for low Deborah number perturbations about Newtonian behavior. The extent to which in-

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