JOURNAL OF CATALYSIS 90, 32–39 (1984)

Design Parameters for Temperature-Programmed Desorption from a Packed Bed[1]

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Received February 14, 1984; revised April 20, 1984

A model for temperature-programmed desorption from a packed bed of spherical particles is presented. It is shown that the conclusions and criteria derived in an earlier paper for a slab in a CSTR apply to this experimental configuration as well when the parameters are properly defined (R. J. Gorte, *J. Catal.* **75**, 164, 1982). Dimensionless groups of easily measured catalyst parameters are presented which enable the experimenter to determine when complications due to readsorption, concentration gradients in the particles, lag times due to diffusion and hold-up in the sample cell, and gradients along the length of the catalyst bed are important. It is shown that the activation energy of the desorption process may not be the heat of adsorption when diffusion in the particles is activated, such as is the case with zeolites. Another important result is that concentration gradients along the length of the bed will be difficult to eliminate without using flow rates high enough to cause gradients in the particles. Conditions for minimizing difficulties and for determining the proper interpretation are given.

INTRODUCTION

Temperature-programmed desorption (TPD) is being increasingly used for characterizing porous catalysts. However, several recent papers have shown that interpretation of the results may be complex, even when the experimental configuration is simple (*1, 2*). These papers have shown that the TPD curves obtained may not be indicative of the desorption kinetics. The coupling of readsorption and mass transfer effects with desorption can raise the peak temperature of the TPD curve several hundred degrees, even when very high carrier-gas flow rates are used. Reick and Bell (*3*) have extended this work by showing that these complications can occur in desorption from packed beds. Their numerical calculations show that, besides readsorption, one must be careful to avoid concentration gradients within the catalyst particles and along the length of the bed.

In this paper, we present a general analysis of desorption from a packed bed. We will show that the dimensionless parameters defined by one of us in a previous paper (*2*) are valid for the packed-bed configuration when the variables are properly defined. In that paper, four parameters were given which could be used to determine the importance of lag times due to flow of adsorbate out of the particles and the sample cell, the importance of concentration gradients in the particles, and the importance of readsorption at high carrier-gas flow rates. Besides showing the validity of these parameters for a packed-bed configuration, two new parameters were determined which indicate the importance of readsorption at low carrier-gas flow rates and of gradients along the length of the bed.

MODEL

We consider the packed bed to consist of N porous spherical particles of radius R, as shown in Fig. 1. The carrier gas flows through the bed and past the particles. Convection through the particles is negligible since the catalyst pores are so small that

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[1] Partially supported by the NSF, Grant CPE-8203968.

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0021-9517/84 $3.00

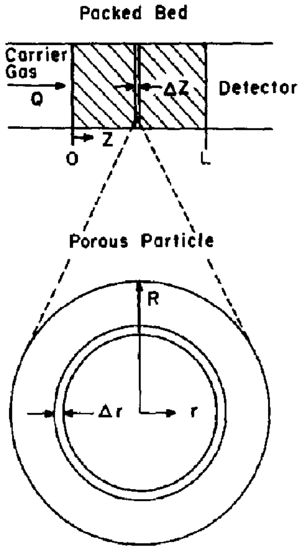

FIG. 1. Schematic representation of the packed-bed sample cell and the enlarged porous particle.

diffusion is much faster. We assume that the particle diameter is small relative to the bed dimensions so that the gas concentration is the same around the entire external surface of the particle. Mass transfer from the edge of the particles to the flowing carrier gas is considered to be fast and radial mixing in the bed is perfect.

With these conditions, we can write material balances on the surface and gas-phase concentrations, n and c, within each individual particle.

Using the dimensionless variables

$$\eta = \frac{r}{R}$$

$$\xi = \frac{z}{L}$$

$$\tau = \frac{\beta}{T_f - T_0} t$$

$$\theta = \frac{n}{n_0}$$

$$v = \frac{c}{\alpha \rho n_0}$$

the equations are

$$\frac{\beta}{T_f - T_0} \frac{\partial \theta}{\partial \tau} = \alpha \rho s F v - k_d \theta \qquad (1)$$

$$\frac{\varepsilon_p R^2 \beta}{D_p (T_f - T_0)} \frac{\partial v}{\partial \tau} = \frac{1}{\eta^2} \frac{\eta}{\partial \eta} \left(\eta^2 \frac{\partial v}{\partial \eta} \right) - \frac{R^2}{D_P} (\alpha \rho s F v - k_d \theta) \qquad (2)$$

These are essentially the same equations that have been analyzed elsewhere (*1–4*). They assume first-order desorption and the ideal gas flux to the surface, Fc. The sticking coefficient, s, can be a function of coverage and temperature. The diffusivity, D_P, may be a function of temperature but is assumed to be independent of concentration.

The surface and gas concentrations are also functions of the dimensionless position of the particle in the bed, defined as $\xi = z/L$. This dependence is determined by the initial and boundary conditions. The initial conditions for all η are at

$$\tau = 0, \qquad \theta = 1, \qquad (3)$$

and

$$v = 0 \qquad (4)$$

The boundary conditions for each particle are at

$$\eta = 0, \qquad \eta^2 \frac{\partial v}{\partial \eta} = 0 \qquad (5)$$

at

$$\eta = 1, \qquad \frac{\varepsilon_B V}{Q} \frac{\beta}{T_f - T_0} \frac{\partial v}{\partial \tau} = - \frac{\partial v}{\partial \xi} + \frac{V}{Q} \frac{D_B}{L^2} \frac{\partial^2 v}{\partial \xi^2} + \frac{4\pi R^2 N D_P}{QR} \left(- \frac{\partial v}{\partial \eta} \right) \qquad (6)$$

where at

$$\xi = 0, \qquad v - \frac{V}{Q} \frac{D_B}{L^2} \frac{\partial v}{\partial \xi} = 0 \qquad (6a)$$

at

$$\xi = 1, \qquad \frac{\partial v}{\partial \xi} = 0 \qquad (6b)$$

The term $(VD_B/QL^2)/(\partial^2 V/\partial \xi^2)$ represents the back-mixing of the carrier gas. D_B is a dispersion coefficient which takes into account fluid mixing as well as diffusion. Correlations can be found for calculating D_B (*5*, *6*).

To determine the importance of concentration differences along the length of the bed, we will analyze the two limiting cases for axial dispersion. When there is perfect back-mixing, Eq. (6) is replaced by the equation for a continuous stirred-tank reactor (CSTR), at

$$\eta = 1\ (\text{CSTR}),\quad \frac{\varepsilon_B V}{Q}\frac{\beta}{T_f - T_0}\frac{\partial v}{\partial \tau} = -v + \frac{4\pi R^2 N D_P}{QR}\left(-\frac{\partial v}{\partial \eta}\right) \tag{7}$$

With this boundary condition, Eqs. (1)–(5) are identical to those equations analyzed in previous papers (*1*, *2*). The only difference is that the area available for diffusion out of the solid is replaced by $4\pi R^2 N$, the external surface area of all the particles in the bed. When there is no back-mixing, Eq. (6) reduces to the equation for a plug flow reactor (PFR) at

$$\eta = 1\ (\text{PFR}),\quad \frac{\varepsilon_B V}{Q}\frac{\beta}{T_f - T_0}\frac{\partial v}{\partial \tau} = -\frac{\partial v}{\partial \xi} + \frac{4\pi R^2 N D_P}{QR}\left(-\frac{\partial v}{\partial \eta}\right) \tag{8}$$

where

$$\xi = 0, \qquad v = 0 \tag{8a}$$

In this dimensionless form, several parameters become apparent. We will next discuss these parameters and show their significance.

RESULTS

The important parameters for TPD from a packed bed are listed in Table 1. Four of these have been discussed in a previous paper for a CSTR configuration (*2*); however, they are applicable to a packed bed as well, regardless of the importance of axial mixing. Two new parameters are also listed which indicate the importance of readsorption at low carrier-gas flow rates and the extent of axial mixing.

The group $\varepsilon_B V\beta/Q(T_f - T_0)$ is the ratio of the average residence time of the carrier-gas, $\varepsilon_B V/Q$, to the time span of the experiment $(T_f - T_0)/\beta$. If this parameter is greater than 0.01, the concentration measured at the reactor exit does not reflect the rate of desorption. Gas molecules desorbing simultaneously from different parts of the bed are detected at different times. This problem must be considered but is easy to avoid experimentally.

TABLE 1

Parameter	Definition	Observed effect	Ideal requirement
$\frac{\varepsilon_B V\beta}{Q(T_f - T_0)}$	Residence time of carrier gas	Convective lag	Must be <0.01 for negligible lag
$\frac{\varepsilon_P R^2\beta}{D_P(T_f - T_0)}$	Time constant for diffusion out of an individual particle	Diffusive lag	Must be <0.01 for negligible lag
$\frac{QR}{4\pi R^2 N D_P}$[a]	Ratio of carrier-gas flow rate to rate of diffusion	Particle concentration gradients	Must be <0.05 for negligible gradients
$\frac{QL^2}{VD_B}$	Ratio of carrier-gas flow rate to axial mixing	Bed concentration gradients	Must be <0.1 for CSTR
$\frac{\alpha\rho sFR^2}{\pi^2 D_P}$	Ratio of adsorption rate to diffusion rate	Readsorption at infinite flow rate	Must be <1 for negligible readsorption
$\frac{\alpha\rho sFV(1 - \varepsilon_B)}{Q}$	Ratio of adsorption rate to carrier-gas flow rate	Readsorption at low flow rate	Must be <1 for negligible readsorption

[a] Total surface area $4\pi R^2 N = 3W/\rho R$.

The parameter describing time lags due to intraparticle diffusion is $\varepsilon_p R^2 \beta / D_p(T_f - T_0)$. This group is the ratio of the diffusion time constant to the time span of the experiment. The time constant is the quantity of gas in a particle, $\frac{4}{3}\pi R^3 \varepsilon_p c$, divided by the characteristic rate of diffusion, $4\pi R^2 D_p(c/R)$. Like the dimensionless residence time for the carrier gas, this parameter should be kept less than 0.01. It cannot be used to determine the importance of concentration gradients within the particle.

The importance of concentration gradients in the catalyst particles is determined by the value of $QR/4\pi R^2 N D_P$. This is the ratio of the rate of adsorbate removal by the carrier gas, Qc, to the characteristic rate of diffusion. Concentration gradients will be significant when this parameter is greater than 0.05. If it is greater than 10, the flow rate may be considered infinite since the mass transfer process is then diffusion limited. While this criterion is strictly true only for the CSTR limit, it is reasonably accurate even under plug flow conditions. In a PFR, some gradients will always exist in the particles at the bed entrance, but the fraction of the bed for which this is important will be negligible when this parameter is small.

When high carrier-gas flow rates are used and desorption is diffusion limited, readsorption is important if the characteristic adsorption rate, $\frac{4}{3}\pi R^3 \alpha p s F c$, is greater than the intraparticle diffusion rate, $4\pi R^2 D_P(c/R)$. If $\alpha p s F R^2 / \pi^2 D_P$ is greater than unity, readsorption will be important even for infinite carrier-gas flow rates. When flow rates of the carrier gas are low enough so that no gradients are present in the particles, the importance of readsorption is determined by the ratio of the adsorption rate to the rate of adsorbate removal with the carrier gas, $\alpha p s F V(1 - \varepsilon_B)/Q$. These parameters are frequently much greater than one, indicating that readsorption can often significantly increase the observed peak temperature.

The final parameter, QL^2/VD_B, is the Péclet number. It determines the extent of back-mixing in the packed bed. When this number is less than 0.1, the bed can be adequately modeled as a CSTR (*5, 6*). Since the measured concentration in a TPD curve is proportional to the rate of desorption only for the CSTR equation, it is very important that this criterion be met. According to correlations by Butt (*5*), it may be very difficult or impossible to accomplish this. The high flow rates necessary to make QL^2/VD_B small by increasing the back-mixing may cause gradients in the particles.

CALCULATIONS

CSTR Limit

The equations in the CSTR limit are identical to those presented in previous papers (*1, 2*) and the analysis will be the same. The only difference is that the area for diffusion out of the catalyst is identified as the external area of the particles in the bed, $4\pi R^2 N$. This area can be easily evaluated from the weight of the bed, W, by

$$4\pi R^2 N = 3W/\rho R \tag{9}$$

It is important to notice that this area will increase with the size of the bed but decrease as the particle size is increased. Decreasing the size of the bed, a test sometimes used for determining the importance of readsorption, can lead to concentration gradients according to the criterion presented here.

PFR Limit

The only difference between the PFR and CSTR limits is in the boundary condition at $\eta = 1$. Consequently, all of the dimensionless parameters important for the CSTR model apply to the PFR as well. The difference in the models results in a difference in the interpretation of $QR/4\pi R^2 N D_P$, the parameter that determines the existence of concentration gradients in the particles.

To determine the criterion for the existence of concentration gradients in the particles of a PFR, we will follow the same procedure as had been used for the CSTR in a previous paper (2). If we assume the lag $\varepsilon_B V\beta/Q(T_f - T_0)$ is small, the equation for the PFR reduces to

$$\eta = 1, \quad \frac{\partial v}{\partial \xi} = \frac{4\pi R^2 N D_P}{QR}\left(-\frac{\partial v}{\partial \eta}\right) \tag{10}$$

If desorption occurs evenly throughout the bed,

$$\left.\frac{\partial v}{\partial \xi}\right|_{\eta=1} \approx \frac{v(\eta = 1)}{\xi} \tag{11}$$

When readsorption occurs at different rates along the bed, this will not be exactly true; however, this approximation is useful for illustration. Substituting this into Eq. (10) gives at

$$\eta = 1, \quad \frac{1}{v}\left(-\frac{\partial v}{\partial \eta}\right) = \frac{1}{\xi}\frac{QR}{4\pi R^2 N D_P} \tag{12}$$

For order of magnitude purposes,

$$\left.\frac{1}{v}\left(-\frac{\partial v}{\partial \eta}\right)\right|_{\eta=1} \approx \frac{v(\eta = 0) - v(\eta = 1)}{v(\eta = 1)} \tag{13}$$

Therefore, $1/v(-\partial v/\partial\eta)|_{\eta=1}$ is a measure of the concentration gradients in the particle. If the readsorption is important, as it usually is, the rate of readsorption will change considerably from the center to the edge of the particle if the concentrations are significantly different. We arbitrarily choose that this concentration gradient should be less than 5%. From Eq. (12), one can see that, unlike for the CSTR, the importance of gradients depends on the position in the bed, ξ.

At the entrance to the bed, where ξ is small, there will always be gradients. This is due to the fact that the first particles will have zero concentration at their boundaries. Therefore, the criterion for preventing concentration gradients should be more conservative for the PFR than for the CSTR. However, this will affect only a small portion of the bed. Also, some backmixing will always occur in practice and it seems unnecessary to make the criterion more conservative. Since it is difficult to determine $QR/4\pi R^2 N D_p$ to better than within a factor of two, one should not perform experiments too closely to this limiting condition. Therefore, the condition for determining the importance of gradients in the particles of a packed bed is the same as presented in a previous paper, whether or not the system acts as a CSTR.

High Flow Rate

For values of $QR/4\pi R^2 N D_p$ greater than 10, desorption is diffusion limited for both the CSTR and PFR cases. At these conditions, the CSTR and PFR are identical because the concentration outside the particles approaches zero for both. In a previous paper (2) it was shown that, for first-order desorption with a coverage-independent sticking coefficient, the effective desorption rate constant is

$$k_{\text{eff}} \approx \frac{k_d}{1 + \dfrac{\alpha \rho s F R^2}{\pi^2 D_P}} \tag{14}$$

If $\alpha\rho sFR^2/\pi^2 D_p$ is much less than 1, the effective rate constant is the true rate constant, k_d. If $\alpha\rho sFR^2/\pi^2 D_p$ is greater than 10, as is often the case, the effective rate constant is

$$k_{\text{eff}} \approx \frac{\pi^2 D_P}{\alpha \rho s F R^2} k_d \tag{15}$$

When Eq. (15) applies, techniques used to analyze the desorption rate, such as varying the heating rate or making Arrhenius plots of desorption rates at constant coverage, will measure the activation energy of k_{eff}. If D_p or s is activated, such as may be the case for zeolites or small pore adsorbants, the measured rate constant will have a reduced preexponential and an activation energy that is the sum of the activation energies of k_d, D_p, and $1/s$.

In most cases, desorption is not ideal first or second order. The activation energy for desorption is frequently a function of coverage. When gradients are present in the particles, the coverage variation from inner to outer parts of the particles will clearly make the TPD curves too complex to analyze. Because of this, these high flow rate conditions should be avoided when possible.

Low Flow Rate

When the lag time due to hold up of adsorbate in the sample cell is negligible and there are no gradients in the particles (low Q), the TPD curve for a CSTR can be analyzed in the way suggested by Cvetanovic and Amenomiya (7). Equation (7) becomes

$$v = \frac{(1 - \varepsilon_B)V}{Q}(k_d - \alpha\rho s F v) \quad (16)$$

In this case, the effective desorption rate constant is

$$k_{\mathrm{eff}} = \frac{k_d}{1 + \dfrac{\alpha\rho s F V(1 - \varepsilon_B)}{Q}} \quad (17)$$

When $\alpha\rho s F V(1 - \varepsilon_B)/Q$ is much less than 1, the effective rate constant has the true value of k_d. When $\alpha\rho s F V(1 - \varepsilon_B)/Q$ is large, which is usually the case, the rate constant becomes

$$k_{\mathrm{eff}} \approx \frac{Q}{\alpha\rho s F V(1 - \varepsilon_B)} k_d \quad (18)$$

which is smaller than k_d.

For a PFR, desorption may not occur evenly along the length of the bed due to the changing concentration with position in the bed. Also, the concentration is not simply proportional to the desorption rate. The applicable equation for a PFR with negligible intraparticle gradients is

$$\frac{\partial v}{\partial \xi} = \frac{(1 - \varepsilon_B)V}{Q}(k_d\theta - \alpha\rho s F v) \quad (19)$$

at

$$\xi = 0, \qquad v = 0 \quad (19a)$$

A simple effective desorption rate constant cannot be calculated from this.

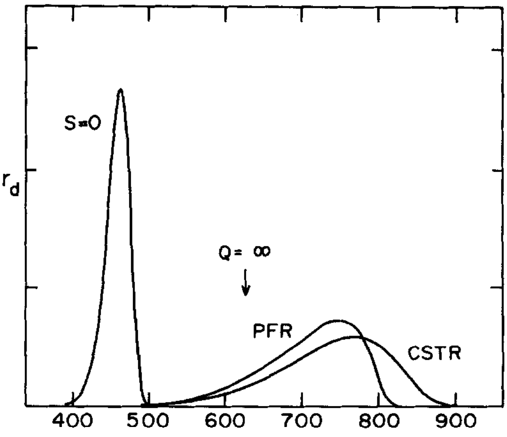

FIG. 2. Calculated TPD curves for desorption from a porous catalyst in a packed bed using the parameters $\alpha\rho = 1.6\ \mathrm{m^2/cm^3}$, $F = [RT/2\pi(28\ \mathrm{g/mole})]^{1/2}$, $S = 1 - \theta$, $k_d = 10^{13} \exp(-30)\ \mathrm{kcal/mole}/RT)/\mathrm{s}$, $\varepsilon_B V = 0.01\ \mathrm{cm^3}$, $Q = 1\ \mathrm{cm^3/s}$, $\varepsilon_p = 0.58$, $D_P = 0.066(T/300\ \mathrm{K})^{1/2}\ \mathrm{cm^2/s}$, $R = 0.01$ cm. The PFR and CSTR limits are shown for the case where concentration gradients do not exist within the particles. The peak temperature for the infinite flow rate limit is indicated by the arrow. This shows that readsorption is important at all flow rates.

To determine the importance of the differences between a CSTR and PFR, we have solved Eqs. (16) and (19) numerically for typical catalyst parameters. The resulting TPD curves are shown in Fig. 2. The TPD curve for both at zero readsorption is shown for reference. Also, the peak temperature for infinite Q, the diffusion limited case, is indicated by the arrow. For this example, readsorption cannot be eliminated by high Q.

As expected, readsorption shifts the peak temperature considerably. The peak temperature for the PFR is slightly lower than for the CSTR. This will be true in general, since the PFR will tend to flush adsorbate from the particles at the entrance to the bed. More important, the shape of the curve from the PFR is considerably different from the CSTR and analysis which assumes that the measured concentration is proportional to the desorption rate will be in error. As with the situation when gradients exist in the particles, desorption in a PFR does not occur evenly throughout the bed and serious problems will occur when desorption is not simple first order.

Dispersion

Since desorption from a PFR can be difficult to analyze, it is important to know the extent of backmixing in the reactor and to determine when the CSTR model is valid. For the dispersion model, the analogous equation to (10) is at

$$\eta = 1, \quad -\frac{VD_B}{QL^2}\frac{\partial^2 v}{\partial \xi^2} + \frac{\partial v}{\partial \xi} = \frac{4\pi R^2 N D_P}{QR}\left(-\frac{\partial v}{\partial \eta}\right) \qquad (20)$$

at

$$\xi = 0, \quad v - \frac{VD_B}{QL^2}\frac{\partial v}{\partial \xi} = 0 \qquad (20a)$$

at

$$\xi = 1, \quad \frac{\partial v}{\partial \xi} = 0 \qquad (20b)$$

When VD_B/QL^2 is greater than 10, this equation predicts the same desorption curve as would be obtained for the CSTR.

Since D_B is a dispersion coefficient which takes into account fluid mixing as well as diffusion, one must use correlations to calculate this parameter. These can be obtained from other sources (*5*, *6*). It is important to note that very high flow rates are needed to make VD_B/QL^2 greater than 10, since D_B is a strong function of Q. In fact, the correlation given by Butt does not extend to flow rates high enough for this to occur. Also, the use of high flow rates will lead to concentration gradients in the particles themselves, a situation which, as we stated previously, should be avoided. Rieck and Bell (*3*) have suggested that this problem can be avoided by using very short beds, only several particle sizes in length. While this will work, care must be taken so that the weight of the bed is not so small that even low flow rates cause gradients in the particles.

SUMMARY

From the governing equations and the above discussion, it can be seen that the parameters defined and discussed previously for the CSTR (*2*) can be applied in the same way to the packed-bed reactor. It has been found that equilibrium readsorption will often occur in the desorption process. Because of this, it is important to avoid concentration gradients, both radial gradients within the particle and axial gradients in the bed. To avoid gradients within the particle, one must run the experiment with a low carrier-gas flow rate. Under these conditions, a new parameter which determines when readsorption will be important can be defined. To avoid axial concentration gradients in the bed, the Péclet number must be considered. Correlations indicate that complete back-mixing may not be possible without inducing concentration gradients within the particles.

APPENDIX: NOMENCLATURE

N	number of particles in the bed
R	radius of the particles
n,θ	adsorbate coverage
c,v	gas-phase concentration
s	sticking coefficient
k_d	desorption rate constant
k_{eff}	effective desorption rate constant
ε_P	particle porosity
ε_B	bed porosity
D_P	particle diffusion coefficient
D_B	bed dispersion coefficient
α	particle surface area (m^2/g)
ρ	particle density
L	bed length
V	bed volume
W	bed weight
Q	carrier-gas flow rate
β	heating rate (K/sec)
T_0	initial temperature
T_f	final temperature
F	$(RT/2\pi M)^{1/2}$ (cm/sec)

ACKNOWLEDGMENT

We are grateful to Professor Douglas A. Lauffenburger for helpful discussions.

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