JOURNAL OF CATALYSIS 75, 164–174 (1982)

Design Parameters for Temperature Programmed Desorption from Porous Catalysts[1]

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Received August 24, 1981; revised January 8, 1982

A model for temperature programmed desorption from porous catalysts is analyzed to determine when concentration gradients are present, when lag time due to diffusion or sample-cell detection is important, and when readsorption affects the spectrum. Dimensionless groups of catalyst parameters were determined which allow a priori calculation of which effects are important and show how to change the experiment to avoid difficulties in interpretation. Concentration gradients are shown to be due mainly to carrier-gas flow rates and may be difficult to avoid. Readsorption can easily change the desorption temperature by several hundred K and cannot be eliminated by increasing the carrier-gas flow rate. Lag times due to pressure build up in the catalyst and to sample-cell detection are shown to be particularly serious since they can affect the heat of adsorption calculated using variable heating rate methods. The analysis shows that great care should be taken in interpreting temperature programmed desorption results and, in many cases, only qualitative features can be obtained.

INTRODUCTION

Temperature programmed desorption (TPD) on supported catalysts is often used to characterize adsorbate systems. However, because the shape and position of the TPD spectra can be affected by diffusional resistances, readsorption, and flow rates of the carrier gas, as well as desorption kinetics, the interpretation is often difficult. Different methods have been suggested for separating these effects by observing the resulting spectra but no method of predicting which rate process is limiting has been developed. Methods that have been developed are often difficult to use; and, as we will show later, they sometimes do not give the correct answer. For example, Cvetanovic and Amenomiya have suggested that varying the flow rate of the carrier gas will determine when the readsorption is important (*1*). Not only is this experimentally difficult in many cases, but we will show that it is not informative. Others have suggested that shape analysis of the desorption spectra will determine the desorption or equilibrium kinetics (*2, 3*). However, even neglecting the effects of diffusion (*4*), backmixing of the carrier gas, and desorption from different size particles and crystal planes, one has the problem that desorption spectra on single crystals rarely have the classical first- or second-order shape suggested by Redhead (*5*). Even for nondissociative adsorption with noninteracting molecules, King (*6*) and Gorte and Schmidt (*7*) have shown that desorption kinetics may not be well described by a simple *n*th-order process. Therefore shape analysis can lead to erroneous conclusions when used to determine which process is rate limiting.

In this work, we have examined a very general model of a porous catalyst, taking into account diffusion, readsorption, and carrier-gas flow rates. By nondimensionalizing this model, we show which parameters are important for giving the different limiting cases and show the solutions of these different cases. This allows a priori prediction of which rate processes will be important in the desorption spectrum and shows how to design the experiment for

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[1] Supported by NSF-DMR-7923647.

0021-9517/82/050164-11$02.00/0

easiest interpretation. An important conclusion is that readsorption must often be considered, even for desorption into a vacuum.

THE MODEL

The model we present is similar to that of Herz *et al.* (*8*). For simplicity, we consider only first-order desorption and we picture the catalyst as a slab of thickness l with uniform porosity, ϵ. The surface area capable of adsorbing gas per volume of catalyst is $\alpha\rho$, the external surface area of the sample is A, and the effective diffusivity is D. The experimental system is pictured in Fig. 1. We neglect lag times due to detector and thermocouple response since these have been shown to be easily avoided (*9*). Other parameters are defined in the Appendix.

The differential mole balance on the gas and surface concentrations, c and n, give Eqs. (1) and (2).

$$\frac{\partial c}{\partial t} = \frac{D}{\epsilon}\frac{\partial^2 c}{\partial x} + \frac{\alpha\rho}{\epsilon} k_d n - \frac{\alpha\rho sFc}{\epsilon}, \qquad (1)$$

$$\frac{\partial n}{\partial t} = -k_d n + sFc. \qquad (2)$$

The sticking coefficient, s, may be a function of temperature or coverage; therefore, the adsorption rate expression, sFc, is completely general. The following boundary and initial conditions must also be satisfied:

$$\text{at } t = 0, \qquad c = 0 \text{ and } n = n_0, \qquad (3)$$

$$\text{at } x = 0, \qquad \frac{\partial c}{\partial x} = 0, \qquad (4)$$

at $x = \frac{l}{2}$,

$$V\frac{\partial c}{\partial t} = -Qc + A\left(-D\frac{\partial c}{\partial x}\right). \qquad (5)$$

Equation (5) is the boundary condition assuming that the sample chamber can be modeled as a stirred tank (*10*). If we define r_d and r_a as the desorption and adsorption rates averaged over the entire surface, then

$$A\left(-D\frac{\partial c}{\partial x}\right)\bigg|_{x=l/2} = \alpha\rho Al(r_d - r_a).$$

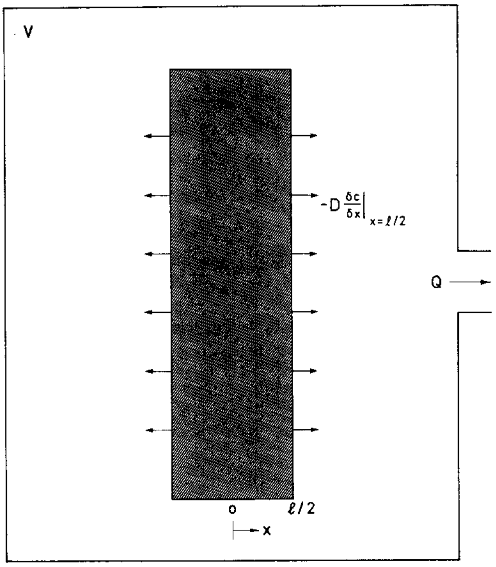

FIG. 1. Schematic representation of the sample cell with a porous catalyst slab. The sample cell is pictured as a well-stirred tank of volume V being pumped at a rate Q.

For small V, Eq. (5) reduces to the equation used by Cvetanovic and Amenomiya (*1*)

$$Qc = \alpha\rho Al(r_d - r_a). \qquad (6)$$

It is important to notice that the sample-cell concentration, $c|_{x=l/2}$, is the parameter that is measured in TPD. The rates r_d and r_a will be independent of position in the sample only if $\partial c/\partial x$ is small enough so that the concentration is constant throughout the pellet or if readsorption is negligible.

Another way of looking at this desorption system is as desorption from uniform pores of radius r and length l. The equations describing this system will be identical except $\alpha\rho/\epsilon$ will be replaced by $2/r$ and s will be decreased by the fraction of surface that is active, to take into account that collisions with inactive surface will not lead to readsorption. This way of looking at the system has the advantage of being easier to picture physically and all results will be identical in form.

We now introduce the dimensionless parameters:

$$Y = (T - T_0)/(T_f - T_0),$$

$$\theta = n/n_0,$$

$$v = Fc/k_{dp}n_0,$$

and

$$g = x/l.$$

That these parameters are scaled properly is obvious for all except v. We note that v is dimensionless and that all scaling factors for v will cancel when we normalize the TPD spectra. The value of k_{dp} is constant and will in no way affect our results since it will cancel out later.

Substituting these parameters into Eqs. (1)–(5) along with the heating schedule $T = T_0 + \beta t$ gives Eqs. (7)–(11)

$$\frac{\beta l^2 \epsilon}{(T_f - T_0)D}\frac{\partial v}{\partial Y} = \frac{\partial^2 v}{\partial g^2} + \frac{\alpha\rho k_d F l^2}{k_{dp}D}\theta - \alpha\rho\frac{sFl^2}{D}v, \quad (7)$$

$$\frac{\beta}{(T_f - T_0)}\frac{\partial \theta}{\partial Y} = -k_d\theta + k_{dp}sv, \quad (8)$$

$$\text{at } Y = 0, \quad v = 0 \text{ and } \theta = 1, \quad (9)$$

$$\text{at } g = 0, \quad \frac{\partial v}{\partial g} = 0, \quad (10)$$

$$\text{at } g = 0.5, \quad \frac{V\beta}{Q(T_f - T_0)}\frac{\partial v}{\partial Y} = -v + \frac{AD}{Ql}\left(-\frac{\partial v}{\partial g}\right). \quad (11a)$$

It is now possible to determine the size of the dimensionless groups that will give different limiting cases and to determine when carrier-gas flow rates, diffusional limitations, and readsorption are important.

SUMMARY

Equations (7)–(11a) have analytical solutions depending on the size of the various dimensionless parameters. The magnitudes of the dimensionless groups which lead to concentration gradients, pressure buildup in the catalyst, sample-cell lag, and readsorption are summarized in Table 1. The manner

TABLE 1

Summary of Catalyst Parameters and Their Effect

Parameter	Physical description	Comments	Significance
$\frac{V\beta}{Q(T_f - T_0)}$	Average residence time for the sample cell	Lag time for sample measurement	Should be kept less than 0.01 for cell concentration to follow net rate of desorption
$\frac{\beta l^2\epsilon}{(T_f - T_0)D}$[a]	Accumulation of gas in the catalyst pore	Lag time for gas to diffuse out of the pore	Should be kept less than 0.01 for cell concentration to follow net rate of desorption
$\frac{Ql}{DA}$[a]	Effect of carrier-gas flow rate	Determines when concentration gradients are present	When <0.1, concentration gradients are negligible. When >20, flow rate is essentially infinite and the concentration at the catalyst edge is effectively zero
$\frac{\alpha\rho sFl^2}{\pi^2 D}$[a]	Ratio of adsorption to diffusion rates for infinite carrier-gas flow rates	Determines when readsorption is important	When >1, readsorption is important, even at high carrier-gas flow rates

[a] For spherical catalyst pellets, replace l by R.

in which each of these limits was determined is given in the Calculations section.

The lag time for the sample cell, $V\beta/Q(T_f - T_0)$, is caused by pressure buildup in the cell. This is the dimensionless space time of the CSTR sample cell; and, if it is large, there will be broadening of sharp desorption peaks and an apparent shift upward in the desorption temperature. Also, the area under the desorption curve will not be proportional to coverage if this is large. This can be easily avoided experimentally by decreasing the volume of the cell or increasing the carrier gas flow rate.

The lag due to accumulation of gas in the sample, $\beta l^2\epsilon/(T_f - T_0)D$, is caused by desorption being greater than diffusion out of the sample. This results in a pressure buildup inside the catalyst which can cause a lag in the detection of the desorbing gas. This has been shown by others to be unimportant in most cases (*2*). This, along with the sample-cell lag, can be reduced by judicious choice of experimental parameters. If they are not eliminated, these lags are serious since they can cause errors when one tries to calculate heats of adsorption by plotting ln β/T_p^2 versus $1/T_p$ (*1*).

Concentration gradients in the sample are controlled by the ratio of the carrier-gas flow rate to the diffusivity, Ql/AD. For large flow rates, the concentration will vary significantly over the width of the catalyst. One cannot assume that high flow rates will make concentrations low enough to allow one to neglect readsorption since flow out of the catalyst will be limited by diffusion. Low flow rates can be used to eliminate concentration gradients but readsorption will become even more important when this is done. Working in intermediate regimes between these two limiting cases should probably be avoided.

When the sticking coefficient is considered independent of θ, the equations can be solved analytically to obtain a criterion for when readsorption is important. This criterion is for infinite carrier-gas flow rate and therefore represents the maximum value for s for which readsorption can be neglected. Lower flow rates will make readsorption more important. The criterion allows s to have a temperature dependence. Therefore, if s is known as a function of temperature, the criterion can be used to determine the temperature region where readsorption becomes important. Comparison of numerical solutions of curves with $s = s_0$ and $s = s_0(1 - \theta)$ shows that this criterion is also good for $(1 - \theta)$ adsorption kinetics.

While the model in this paper is for a rectangular geometry, we have also solved the problem for a spherical catalyst pellet to see the effect this geometry would have on the results. The results in Table 1 were identical if we replace l by R, the radius of the spherical pellet. Therefore, the groups presented in Table 1 can be used for spherical geometry as well as rectangular.

CALCULATIONS

In this section, we develop the criteria presented in Table 1.

Sample Cell, Lag Time

In TPD, we wish to measure the net rate of desorption. By comparing Eqs. (6) and (11), we see that this is proportional to $(\partial v/\partial g)|_{g=0.5}$. With the sample cell modeled as a stirred tank, the term

$$\frac{V\beta}{Q(T_f - T_0)} \frac{\partial v}{\partial Y}$$

in Eq. (11) gives a lag time in the concentration measurements. The average residence time of the sample cell is the lag time constant and is given by

$$\frac{V\beta}{Q(T_f - T_0)}.$$

We stipulate that a temperature lag of 5 K or less will be unimportant. Therefore, for a typical 500 K scan ($T_f - T_0 = 500$ K), the lag time will be important if

$$\frac{V\beta}{Q(T_f - T_0)} > 0.01. \qquad \text{(I)}$$

If relation I holds, the concentration in the cell will not accurately follow the net rate of desorption. As mentioned earlier, experimenters should take care to avoid the situation where relation I is true and we will not consider this case further. With this term negligible, the cell concentration will be proportional to the net rate of desorption and Eq. (11a) reduces to

$$\text{at } g = 0.5, \qquad v = \frac{AD}{Ql}\left(-\frac{\partial v}{\partial g}\right). \tag{11b}$$

Concentration Gradients

If Ql/AD is small, $-((1/v)(\partial v/\partial g))_{g=0.5}$ is also small. Since $(\partial v/\partial g)|_{g=0}$ is always zero from our boundary condition, this is the case where there are no significant gas phase concentration gradients in the pellet. Physically, we know that the concentration is maximized at the center of the slab ($g = 0$) and minimized at the edge ($g = 0.5$). The concentration gradient, on the other hand, is zero in the center and a maximum at the edge. If $Ql/AD = 0.1$, we see that, even if the concentration gradient were at its maximum throughout the pellet, the concentration would vary by only 5% from the center to the edge. Therefore, there will be no significant concentration gradients for

$$\frac{Ql}{AD} < 0.1. \tag{II}$$

With no concentration gradients present, the rates of adsorption and desorption will not be a function of position inside the pore and the operational equation will be Eq. (6). In this case, the analysis by Cvetanovic and Amenomiya (*1*) is applicable. We shall show in the next two sections that, except for low sticking coefficients, adsorption–desorption equilibrium is reached even for desorption in a vacuum. It is, therefore, usually reached in this low flow rate limit. This case is treated by Cvetanovic and Amenomiya (*1*) for a Langmuir isotherm with negligible sample-cell lag to give

$$\frac{dn}{dt} = \frac{Q}{\alpha \rho A l} K \frac{n}{n_0 - n} \tag{12}$$

for an equilibrium constant, K. In this case, measurement of the peak temperatures as a function of β will allow one to determine a heat of adsorption, but preexponentials should not be assumed. Also, in this limit, the peak temperature will be a function of the carrier-gas flow rate, although not a very strong function (*8*).

Before considering the high carrier-gas flow rate limit, we note that there can be a problem with keeping the flow rate low enough so that relation II is followed. A is the external area of the sample and will typically be about 1 cm^2. Letting D be 0.01 cm^2/sec, and l be 0.01 cm, Q needs to be less than 0.1 cm^3/sec for relation II to hold. For flow rates greater than this, concentration gradients begin to be important. Since this is a very low flow, it may be difficult to avoid gradients in some cases.

High Carrier-Gas Flow Rates

With high carrier-gas flow rates or when desorption is into a vacuum, Eq. (11) reduces to

$$\text{at } g = 0.5, \qquad v \approx 0. \tag{11c}$$

Now we anticipate that, if readsorption is important, concentration gradients will be present in the pore and the analysis by Cvetanovic and Amenomiya (*1*) is no longer applicable. We will still assume that the net desorption rate from the catalyst is proportional to the concentration as in Eq. (6); however, now adsorption and desorption rates may be different in different parts of the sample. Assuming that the sticking coefficient is independent of coverage, Eqs. (7)–(11b) have an analytical solution. The high flow rate limit given by Eq. (11c) is approached closely for

$$\frac{Ql}{AD} > 20. \tag{III}$$

For flow rates above that given by this relation, the shape of the TPD spectra and the peak temperature are unaffected by further increases in the carrier-gas flow rate. We will now look more closely at this analytical solution, using Eq. (11c) as the boundary condition in place of Eq. (11a), to determine the effects of readsorption and concentration gradients.

Readsorption at High Carrier-Gas Flow Rates

Two assumptions must be made to obtain a closed-form, analytical solution. First, we assume the sticking coefficient is independent of surface coverage. (The effect of $(1-\theta)$ kinetics is shown later.) The $(1-\theta)$ dependence of Langmuir kinetics and the $\exp(-\gamma\theta)$ dependence of the Elovich equation both reduce to one at low coverages. Therefore, our approximate solution will be identical to the solutions for these other cases at low coverages. Also, for many experimental cases, such as CO on Pt, s does appear to be almost independent of coverage (*11*). We do not make any assumptions about the temperature dependence of s and we do not exclude the possibility of activated adsorption.

The second approximation is to neglect the term

$$\frac{\beta l^2\epsilon}{(T_\mathrm{f}-T_0)D}\frac{\partial v}{\partial \mathrm{Y}},$$

the left-hand side of Eq. (7) (this assumption is unnecessary for the validity of relation (III)). This term represents the pressure buildup inside the catalyst pellet and will be negligible for

$$\frac{\beta l^2\epsilon}{(T_\mathrm{f}-T_0)D} < 0.01. \qquad \text{(IV)}$$

(The number 0.01 was determined in a similar manner as in relation I.) This requirement is essentially that given by Ibok and Ollis (*2*) for limiting diffusional effects. We note that concentration gradients can occur independent of the value of this group. We use the term pressure buildup as a better expression for what this term represents. For catalyst widths of 1 mm and heating rates of 1 K/sec, this dimensionless group will typically be 0.001. Therefore, pressure buildup will usually be negligible and should, in any case, be avoided since the desorption spectrum would then be a function of the response time of the catalyst particle. This approximation does not in any way assume that the concentration is independent of time.

To solve Eqs. (7)–(11), the concentrations are expanded in a Fourier transform.

$$v = \sum_{m=0}^{\infty} Y_m(\mathrm{Y})2^{1/2}\cos\{(2m+1)\pi g\},$$

$$\theta = \sum_{m=0}^{\infty} Z_m(\mathrm{Y})2^{1/2}\cos\{(2m+1)\pi g\}.$$

Substituting these into Eqs. (7) and (8) and integrating with $\cos\{(2m+1)\pi g\}$ gives

$$0 = -\{(2m+1)\pi\}^2 Y_m + \frac{\alpha\rho k_\mathrm{d}}{k_\mathrm{dp}}\frac{Fl^2}{D}Z_m - \frac{\alpha\rho sFl^2}{D}Y_m \qquad (13)$$

and

$$\frac{\beta}{(T_\mathrm{f}-T_0)}\frac{dZ_m}{d\mathrm{Y}} = -k_\mathrm{d}Z_m + k_\mathrm{dp}sY_m. \qquad (14)$$

Rearranging Eq. (13) gives

$$Y_m = \frac{(\alpha\rho Fl^2)/D(k_\mathrm{d}/k_\mathrm{dp})Z_m}{\{[(2m+1)\pi]^2 + \alpha\rho sFl^2/D\}} \qquad (15)$$

and

$$\frac{\beta}{(T_\mathrm{f}-T_0)}\frac{dZ_\mathrm{m}}{d\mathrm{Y}} = \left\{-k_\mathrm{d} + \frac{(\alpha\rho sFl^2/D)k_\mathrm{d}}{\{[(2m+1)\pi]^2 + \alpha\rho sFl^2/D\}}\right\}Z_m = -k_\mathrm{eff}Z_m. \qquad (16)$$

The solution for Eq. (16) is readily obtained, subject to the initial condition in Eq. (9), to give

$$Z_m(\mathrm{Y}) = \frac{(-1)^m 8^{1/2}}{\pi(2m+1)} \times \exp\{\frac{-(T_\mathrm{f}-T_0)}{\beta}\int_0^{\mathrm{Y}} k_\mathrm{eff}d\mathrm{Y}\}. \qquad (17)$$

Notice that no assumptions have been made about the temperature dependence of any of the parameters. The quantity of adsorbate on the catalyst surface at any time is given by

$$2\alpha p A l n_0 \int_0^{0.5} \theta\, dg = \alpha p A l n_0 \sum_{m=0}^{\infty} \frac{8}{\pi^2(2m+1)^2} \times \exp\{-\frac{(T_f - T_0)}{\beta} \int_0^{Y} k_{\text{eff}} dY\}. \quad (18)$$

(It is necessary to integrate over the pore length because concentration gradients can make the coverage a function of position in the pore.) The derivative with respect to time of Eq. (18) is the net rate of desorption that is observed in TPD spectra according to Eqs. (6) and (11b). We will work with the integrated coverage for computational simplicity. Since

$$\sum_{m=0}^{\infty} \frac{8}{\pi^2(2m+1)^2} = 1,$$

Eq. (18) gives the proper limiting case for Y = 0. This also shows that the $m = 0$ term accounts for 81% of the initially adsorbed gas. Therefore, consideration of only the first term will give a good indication of the character of the solution.

A closer examination of Eq. (16) shows that there are two limiting cases. For

$$\frac{\alpha p s F l^2}{D} \ll \pi^2, \quad (\text{V})$$

$k_{\text{eff}} \approx k_d$ and we have the case where there is no readsorption. This situation was analyzed by Redhead (*5*) to give, by direct integration,

$$2 \int_0^{0.5} \theta\, dg \approx \exp\{-\frac{(T_f - T_0)}{\beta} \int_0^{Y} k_d dY\}. \quad (19)$$

Even in this case, a preexponential of 10^{13} sec^{-1} should not be assumed (*15*). For

$$\frac{\alpha p s F l^2}{D} \gg \pi^2 \quad (\text{VI})$$

readsorption is important and Eq. (18) reduces to

$$2.\int_0^{0.5} \theta\, dg \approx \sum_{m=0}^{\infty} \frac{8}{\pi^2(2m+1)^2} \times \exp\{-\frac{(T_f - T_0)}{\beta} [(2m+1)\pi]^2 \times \frac{D}{\alpha p F l^2} \int_0^{Y} \frac{k_d}{s} dY\}. \quad (20)$$

(We have used the fact that $1/(1 + x) \approx 1 - x$ for small x.) Considering only the first term since this accounts for 81% of the desorption area,

$$2 \int_0^{0.5} \theta\, dg \approx \exp\{-\frac{(T_f - T_0)}{\beta} \times \frac{\pi^2 D}{\alpha p F l^2} \int^{Y} \frac{k_d}{s} dY\}. \quad (21)$$

The effective desorption rate constant for the case of readsorption is approximately given by

$$k_{\text{eff}} \approx \frac{\pi^2 D}{\alpha p F l^2 s} k_d. \quad (22)$$

This effective desorption rate constant with readsorption is proportional to k_d/sF, or the desorption rate constant divided by the adsorption rate constant. This is the equilibrium constant and shows that equilibrium between adsorption and desorption is established on this surface. Also, if s is independent of temperature, the effect of readsorption is to change the preexponential of the observed rate constant by a factor of $\pi^2 D/\alpha p s F l^2$, which we have already assumed is less than one. Therefore, the predicted rate constant will have a low preexponential.

Before addressing the question of whether readsorption actually occurs in reality, several points should be made. First, the activation energy for the rate constant in Eq. (22) is still the heat of adsorption. The equation developed by Redhead (*5*) for the peak temperature is still valid,

$$\frac{(-\Delta H)\beta}{R T_p^2} = \frac{\pi^2 D \nu}{\alpha p S_0 F l^2} \times \exp\{-(-\Delta H)/R T_p\}. \quad (23)$$

The peak temperature is now a function of the catalyst width and surface area; however, a plot of $\ln(\beta/T_p^2)$ versus $1/T_p$, as proposed by Cvetanovic and Amenomiya (*1*), is capable of determining the heat of adsorption, even though concentration gradients are present. Also, the peak temperature from Eq. (23) is *independent of carrier-gas flow rate,* even though readsorption is important, showing that varying the flow rate will not help in determining whether readsorption is important. Finally, the effective preexponential for desorption will be low.

Effect of $(1 - \theta)$ *Adsorption Kinetics*

That readsorption can make a dramatic change in the TPD spectrum has already been shown by Herz *et al.* (*8*) and the result of one of their calculations with $s = 0.5(1 - \theta)$ is reproduced in Fig. 2. For comparison, the analytical solution with $s = 0.5$ is also shown. Herz *et al.* included the lag and flow rate effects in their calculations. However, for the parameters they used in the particular calculation shown here, the lag effects are negligible and an infinite flow rate can be assumed. The $s = 0.5$ curve has a peak

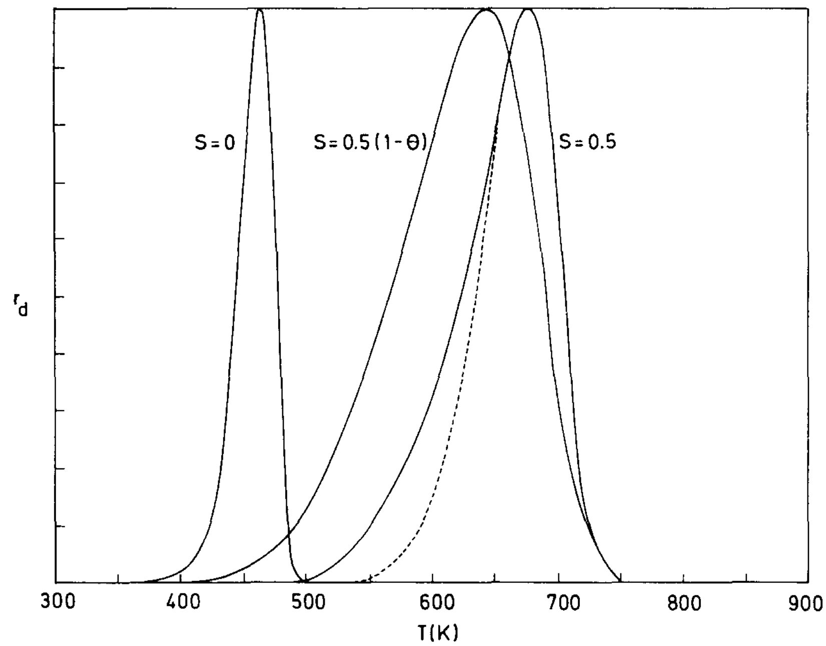

FIG. 2. Calculated TPD spectra for desorption from a porous catalyst. The curves show the effect of different expressions for the sticking coefficient. The $s = 0.5(1 - \theta)$ curve is taken from a computer calculation by Herz *et al.* (*8*) and includes both lag times and the pumping speed effect. The other curves assume infinite pumping speed and no lag effects and were calculated using Eq. (20). In all cases, the TPD spectra were normalized and the initial coverage was one. Other parameters were as follows:

$Q = 2000$ cm³/sec,
$F = (RT/2\pi M)^{1/2}$,
$k_d = 10^{13} \exp\{-30 \text{ kcal/mole}/RT\}$,
$\alpha\rho = 1.6$ m²/cm³,
$D = 0.066\,(T/300)^{1/2}$ cm²/sec,
$l = 0.02$ cm,
$A = 0.8$ cm²,
$\epsilon = 0.58$.
$\beta = 1$ K/sec,
$V = 5$ cm³,
$M = 28$ g/mole.

temperature of 675 K while the $s = 0.5\,(1 - \theta)$ curve has a maximum at 636 K. This lower peak temperature is expected since the $(1 - \theta)$ term will lower the readsorption rate; however, the difference is not very large. If one replaces $(1 - \theta)$ by 0.5 to take into account that the coverage in the peak region is about 0.5, the peak temperature for $s = 0.25$, predicted by Eq. (23), would be 655 K, which is quite close to the $s = 0.5\,(1 - \theta)$ result. This shows that the assumption of a constant sticking coefficient is quite good for calculating the effect that readsorption has on the peak temperature, even when $(1 - \theta)$ kinetics would be more accurate. One should remember, however, that the observed sticking coefficients often do not have a $(1 - \theta)$ dependence and there may be no particular reason to add this complication.

The dashed line in Fig. 2 shows a plot of the first term in the series solution, Eq. (21). The result is to neglect a leading tail on the curve, but the region around the peak temperature is unaffected. This shows that desorption will be described very well by an effective desorption rate constant as in Eq. (22) and proves the validity of Eq. (23).

Evaluation of the Sticking Coefficient

Relation VI gives the parameter region for which readsorption is important when high carrier-gas flow rates are used or desorption is into a vacuum. For very conservative properties such as given in Fig. 2, $\alpha pFl^2s/\pi^2D$ is $(1.2 \times 10^5)s$. Therefore, readsorption will be important for sticking probabilities greater than 10^{-5}. In the case where readsorption is into a carrier gas at lower flow rates and higher partial pressures, quick calculations using Eq. (11b) with $Ql/AD < 0.1$ indicate that s needs to be about two orders of magnitude lower for readsorption to be negligible. While we have an expression for when adsorption is important, a priori determination of s is difficult. For ultrahigh vacuum studies, sticking coefficients must be greater than $\sim 10^{-3}$ in order for a surface to be populated in reasonable time scales, showing that high sticking coefficients are not uncommon. This leads to the conclusion that readsorption is important in very many cases.

An estimation of s may sometimes be difficult to obtain. Halpern and Germain (*12*), using different arguments, developed a criterion essentially identical to relation VI for determining if readsorption is important. Their derivation also implicitly assumed desorption into a vacuum. However, they used a theoretical formula derived from statistical mechanics (*13*) to determine s, and they concluded that readsorption was not important for their system. While this may have been true for their system, we feel that theoretical relations for sticking coefficients should not be used to estimate these values since our understanding of adsorption processes is still limited. A better way to guess sticking coefficients is to assume that s is independent of temperature and observe how long it takes to begin to populate desorption states.

For example, if $s = 10^{-10}$, it will be necessary to expose the surface to about 10^4 Torr sec (an exposure of 100 Torr for 100 sec). Adsorption may also give concentration gradients and s may be a function of temperature; therefore, values of s determined in this way should be considered minimum values. We note that exposures greater than 10^4 Torr sec may take prohibitively long times. Therefore, there will be a fairly narrow range of values for which the sticking coefficient is small enough for readsorption to be negligible and large enough for easy adsorption.

Temperature Programmed Reaction

That readsorption is often important has interesting implications for molecules that can react upon desorption. On the average, each molecule will have to desorb $\alpha psFl^2/\pi^2D$ times, even when the carrier-gas flow rate is infinite. If s is moderately large, each molecule will undergo many desorption and adsorption processes and TPD with reaction will not be much different from running a reaction at the instantaneous pressure and temperature of the desorption. Since this is the case, the experimenter should be careful to address very specific questions about the reaction, which cannot be answered by reactor studies, before using TPD. In many cases, it will be much easier to use reactor studies since the temperature and pressure can be varied independently. Because readsorption is important in many cases, analysis similar to that used on low surface area catalysts should not be used (*14*).

CONCLUSIONS

We have shown that various groups of catalyst parameters can have a large effect in the observed TPD spectrum from porous catalysts. The experimenter should be conscious of these effects and design his experiment to avoid the possible complications. In particular, lag times in the sample cell and in the pore can usually be made negligible. Readsorption, on the other hand, is intrinsic to the adsorption system being studied and often cannot be eliminated by changing experimental parameters. The possibility of readsorption in TPD from porous samples should always be considered since it can raise peak temperatures by several hundred degrees. This should be considered especially when reaction is occurring along with desorption. Finally, our results show that heats of adsorption can be calculated when TPD spectra are taken at different heating rates; however, lag times should be checked to see that they will not interfere with the results and preexponentials should not be assumed.

APPENDIX: NOMENCLATURE

c = gas phase concentration (molecules/cm^3)
n = surface concentration (molecules/cm^2)
n_0 = initial surface concentration
β = heating rate (K/sec)
T_0 = initial temperature
T_f = final temperature
T_p = temperature at maximum desorption
k_d = desorption rate constant (sec^{-1})
= $\nu \exp(-E/RT)$
k_{dp} = desorption rate constant evaluated at $(T_0 + T_f)/2$
Fc = flux of gas to the surface ($F = (RT/2\pi M)^{1/2}$)
s = the sticking coefficient, the probability that a gas molecule striking the surface will adsorb
= $S_0 \exp(-Ea/RT) f(\theta)$
ΔH = heat of adsorption ($\Delta H = Ea - E$)
Q = flow rate of the carrier gas (cm^3/sec)
V = volume of the sample chamber (cm^3)
ϵ = porosity (cm^3/cm^3)
α = active surface area (cm^2/g)
ρ = apparent catalyst density (g/cm^3)
A = external surface area (cm^2)
D = effective diffusivity (cm^2/sec)
l = width of catalyst slab
R = radius of spherical catalyst pellet
r = average radius of catalyst pore
= $2/\alpha\rho$ if all the surface is active

ACKNOWLEDGMENTS

Helpful advice was received from Dr. D. A. Lauffenburger and Dr. C. Takoudis. Thanks are also due Drs. R. K. Herz, J. B. Kiela and S. P. Marin for access to their manuscript before publication.

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