Temperature-Programmed Desorption: Multisite and Subsurface Diffusion Models

Two models are presented that can simulate two peaks in a temperature-programmed desorption (TPD) spectrum from a high surface area catalyst at atmospheric pressure: a multisite model and a subsurface diffusion model. The multisite model assumes that the two peaks arise from two distinct adsorption sites on the catalyst surface with different activation energies for desorption. The subsurface diffusion model assumes that the high-temperature peak is produced by adsorbate that diffuses into the subsurface region of the catalyst during heating, and then back to the surface when it becomes depleted by the desorption process. It is shown that one can distinguish between the two models experimentally by measuring the effect of carrier gas flow rate and heating rate on the TPD spectrum.

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Introduction

Temperature-programmed desorption (TPD) and related techniques are very useful tools for characterizing solid materials. TPD has been used most commonly to study the binding of adsorbates to catalytic surfaces. A schematic picture of a TPD experiment is shown in Figure 1. Initially the catalyst surface is covered with the adsorbate of interest. Then while a carrier gas flows over the sample, the temperature is raised linearly in time. As the catalyst is heated, the adsorbate begins to desorb from the surface into the carrier gas stream from which it can either be readsorbed or be swept out of the reactor. The concentration of the adsorbate in the effluent from the reactor is monitored continuously with a mass spectrometer. If the reactor is well mixed, this concentration is proportional to the net rate of desorption (R_d = desorption rate − readsorption rate) from the surface. Initially the desorption occurs at an increasing rate since it is an activated process. Eventually the surface becomes depleted of adsorbate, and the net desorption rate goes through a maximum and then decreases again, producing a peak in the spectrum. The temperature of this desorption peak is indicative of the strength with which the adsorbate is bound to the surface. In general, the more strongly the adsorbate is bound to the surface, the higher the temperature of the desorption peak. As discussed in more detail later, a quantitative determination of the heat of adsorption can be obtained from the shift in the peak temperature with heating rate. In many cases the surface contains more than one type of adsorption site. If the heats of adsorption on these sites differ significantly, the TPD spectrum will contain multiple peaks, one for each type of adsorption site. When this happens, the heat of adsorption on each type of site can be determined separately, rather than obtaining an average over the entire surface, as is the case in chemisorption studies.

A major advantage of TPD compared to other surface sensitive techniques is that ultrahigh vacuum conditions are not required to study the binding of adsorbates to the catalyst surface. As a result, the catalyst can be studied under conditions that more closely resemble actual catalytic reaction conditions. The application of TPD and related techniques to the study of practical catalysts has been reviewed by Cvetanovic and Amenomiya (1967, 1972), and by Falconer and Schwarz (1983).

It is important to note that multiple peaks in a TPD spectrum do not always indicate the presence of multiple adsorption sites on the catalyst surface. Extra peaks also can be produced by lateral interactions between adsorbate molecules (induced heterogeneity) (Yates, 1985; Tokoro et al., 1979). Furthermore, in two recent studies (Leary et al., 1987a, b) we have shown that the penetration of adsorbates such as hydrogen and oxygen into the subsurface region of a catalyst can produce high-temperature peaks in a spectrum. When this occurs, TPD is a useful technique for studying diffusion in the subsurface region.

One of many applications in which subsurface diffusion might be important is catalysis. Diffusion of one or more reactants into the subsurface region of the catalyst under reaction conditions could affect the way various adsorbates bind to and react on the surface. Therefore, it is important to determine whether an adsorbate can diffuse into the subsurface region of the catalyst to any significant extent. TPD can be a useful tech-

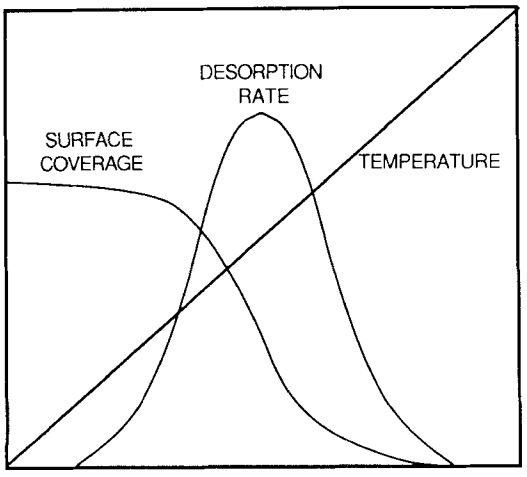


Figure 1. A TPD experiment.

nique for studying subsurface diffusion, but first one must be able to distinguish between a peak caused by subsurface diffusion and one produced by an additional adsorption site.

In this paper we show how to distinguish between these two possibilities experimentally by measuring the effects of carrier gas flow rate and heating rate on the spectrum. This is shown by simulating two-peak TPD spectra with a multisite model and a subsurface diffusion model, and comparing how the spectra change as these parameters are varied. The multisite model presented here assumes that the two peaks are produced by desorption from two distinct adsorption sites, and is similar to the model described by Chin and Bell (1983). The subsurface diffusion model assumes that the surface contains only one type of adsorption site, and that the high-temperature peak is caused by subsurface diffusion of the adsorbate. Once it is determined that a diffusion peak is present in the spectrum, we show that one can estimate the activation energy for diffusion of the adsorbate from the subsurface to the surface from the shift in the diffusion peak temperature with heating rate.

Theory

In both of the models presented here, desorption is taken to occur from a fixed bed of catalyst into a carrier gas stream that flows through the bed. It is assumed that the TPD experiment is performed under conditions for which the Peclet number is small enough that the catalyst bed can be modeled as a continuous-flow stirred-tank reactor (CSTR). Since the measured adsorbate concentration is proportional to the net desorption rate only for a CSTR, it is very important that this requirement be met (Demmin and Gorte, 1984). For reasonable carrier gas flow rates, we also can neglect accumulation of the adsorbate in the reactor (Cvetanovic and Amenomiya, 1967, 1972; Falconer and Schwarz, 1983). This assumption was not made by Chin and Bell (1983) in their multisite model. We also assume that the catalyst particles are small enough that intraparticle diffusion limitations can be neglected. The conditions under which this assumption is valid, and the effects of intraparticle diffusion limitations on TPD spectra have been considered previously (Tronconi and Forzatti, 1985; Rieck and Bell, 1984; Demmin and Gorte, 1984; Gorte, 1982).

Multisite model

In modeling the desorption from a heterogeneous surface, we consider the case where the surface contains two distinct adsorption sites of different binding energies. As the catalyst is heated, the adsorbate desorbs at different rates from each site. This is shown schematically in Figure 2. Since the reactor is well stirred, the adsorbate also can readsorb on either site before it is swept from the reactor by the carrier gas.

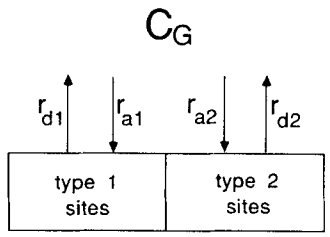
In this model, we do not explicitly consider surface diffusion of the adsorbate from one site to another. This process occurs in parallel with readsorption, and both processes provide a path for transfer of adsorbate between the two sites. Typically, the adsorption and desorption rates in an atmospheric pressure TPD system are several orders of magnitude larger than the net desorption rate. This high rate of exchange of adsorbate between the surface and the gas phase allows for rapid equilibration of the adsorbate between the two sites. For this reason it is not necessary to include surface diffusion in this model. It is important to note that this assumption may not be valid under ultrahigh vacuum conditions.

Mass balances on the adsorbate on each site yield the following expressions.

$$\frac{d\theta_1}{dt} = nk_a(1 - \theta_1)^n C_G - nk_{d1}\theta_1^n \tag{1}$$

$$\frac{d\theta_2}{dt} = nk_a(1 - \theta_2)^n C_G - nk_{d2}\theta_2^n \tag{2}$$

The first term on the righthand side of Eqs. 1 and 2 describes the rate of adsorption from the gas phase, and the second term expresses the rate of desorption of the adsorbate from the surface. It is assumed that adsorption and desorption can be modeled as nth-order processes, with n typically being 1 or 2. In cases where precursor adsorption kinetics are observed, these equations must be modified. The fractional coverage of type 1 and type 2 sites are given by θ_1 and θ_2, respectively.



$$r_{d1} = n\,k_{d1}\theta_1^n$$
$$r_{a1} = n\,k_a\,(1 - \theta_1)^n C_G$$
$$r_{d2} = n\,k_{d2}\theta_2^n$$
$$r_{a2} = n\,k_a\,(1 - \theta_2)^n C_G$$

Figure 2. TPD from a catalyst containing two distinct adsorption sites of differing binding energies.

r_{di}, desorption rate from type i sites
r_{ai}, readsorption rate on type i sites

A mass balance on the reactor yields the following expression for the gas phase concentration of the adsorbate

$$C_G = -\frac{N_S}{nQ}\left(X_1\frac{d\theta_1}{dt} + X_2\frac{d\theta_2}{dt}\right) \tag{3}$$

where N_S is the total number of surface sites, and Q is the carrier gas flow rate. The fraction of sites that are type 1 and 2 are given by X_1 and X_2, respectively. It is important to point out that Eqs. 1 and 2 are coupled through Eq. 3. Therefore, one cannot model desorption from a surface containing two sites by simulating the desorption from each site independently and then simply adding the results.

During a TPD experiment, the carrier gas molar flow rate is held constant, and since the reactor operates isobarically, the volumetric flow is temperature-dependent. Assuming that the gas behaves ideally, the volumetric flow rate varies as

$$Q = Q_0\left(\frac{T}{273}\right) \tag{4}$$

where T is the temperature and Q_0 is the flow rate at 1 atm and 273 K (STP).

The rate constants in Eqs. 1 and 2 also are temperature-dependent according to Eqs. 5 and 6:

$$k_a = S_0\left(\frac{RT}{2\pi m}\right)^{1/2}\sigma \tag{5}$$

$$k_{di} = \upsilon_{di}\exp\left(-\frac{E_{di}}{RT}\right) \tag{6}$$

The expression for the adsorption rate constant in Eq. 5 is derived from kinetic theory. In Eq. 5, m is the molecular weight of the adsorbate and σ is the area occupied by one mole of adsorption sites. It is assumed that the sticking coefficient, S_0, is equal for both sites and is independent of temperature and coverage. We also assume that the adsorption is not activated (Rieck and Bell, 1984). In Eq. 6, the preexponential factors υ_{di} and the desorption activation energies E_{di} are assumed to be constant.

The temperature of the catalyst bed is assumed to be uniform and to vary linearly in time with heating rate β:

$$\frac{dT}{dt} = \beta \tag{7}$$

During adsorption the surface sites fill sequentially, with the highest binding energy sites filling first (Somorjai, 1981). Therefore if the high binding energy sites are denoted as type 2 and the low binding energy sites as type 1, the initial conditions for Eqs. 1, 2, and 7 are

$$\text{at} \quad t = 0, T = T_0 \tag{8}$$

$$\theta_2^{(0)} = \frac{\theta_T^{(0)}}{X_2} \quad \text{and} \quad \theta_1^{(0)} = 0 \quad \text{if} \quad \theta_T^{(0)} < X_2 \tag{9a}$$

$$\theta_2^{(0)} = 1.0 \quad \text{and} \quad \theta_1^{(0)} = \frac{\theta_T^{(0)} - X_2}{X_1} \quad \text{if} \quad \theta_T^{(0)} > X_2 \tag{9b}$$

where $\theta_T^{(0)}$ is the total initial surface coverage, and $\theta_1^{(0)}$ and $\theta_2^{(0)}$ are the initial coverages on the type 1 and type 2 sites, respectively.

Equations 1, 2, and 7 were solved numerically using a fourth-order Runge-Kutta method with variable step size. From these results, the net desorption rate

$$R_d = -\left(X_1\frac{d\theta_1}{dt} + X_2\frac{d\theta_2}{dt}\right) \tag{10}$$

was calculated and plotted as a function of temperature to give the desorption spectrum. Alternatively, one could plot the concentration of the adsorbate in the carrier gas as a function of temperature. These differ only by the factor N_S/nQ.

Figure 3 shows the calculated desorption spectrum from a surface containing equal amounts of two distinct sites as a function of the initial coverage. For these spectra the carrier gas flow rate was 100 cm^3/min (STP) (1 cm^3/min = 1.67×10^{-8} m^3/s), and the heating rate was 1 K/s. The values of the remaining parameters are listed in Table 1 and were chosen to be representative of hydrogen desorption from noble metals (Somorjai, 1981). As seen in Figure 3, the spectrum contains only one peak for $\theta_T^{(0)} \leq 0.5$. This peak corresponds to desorption from the high binding energy adsorption site (type 2). As expected for a second-order desorption process, the peak narrows and shifts to lower temperatures as the initial coverage increases (Rieck and Bell, 1984). Above $\theta_T^{(0)} = 0.5$, the lower binding energy site starts to fill, producing a low-temperature desorption peak.

Subsurface diffusion model

The subsurface diffusion model presented here assumes that the surface contains only one adsorption site whose binding energy is coverage-independent. These results can be extended to cases where the surface contains multiple adsorption sites by combining this model with the multisite model presented above. In the subsurface diffusion model, the adsorbate is allowed to diffuse between the surface and the layers just beneath the surface during the temperature ramp. The layers just beneath the surface are referred to as the subsurface region. It is important to distinguish between the subsurface region and the bulk since diffusion in the subsurface region may be very different from diffusion in the bulk (Leary et al. 1987a). Moreover, in most practical catalysts the dispersion is very high, so the crystallites only contain a few subsurface layers, and there may not be any

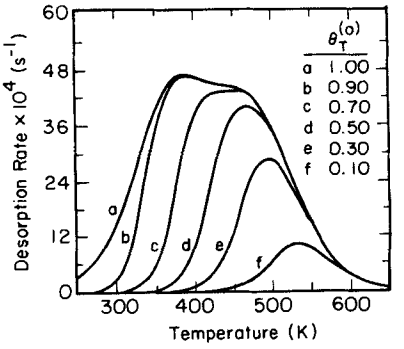


Figure 3. Effect of initial coverage on TPD spectrum simulated by multisite model.

Q_0 = 100 cm^3/min; β = 1.0 K/s; other parameter values as in Table 1

Table 1. Parameter Values Used in Multisite Model

N_S	3.0×10^{-6} mol
m	2.0
n	2.0
S_0	0.005
σ	4.0×10^8 cm^2/mol (4.0×10^4 m^2/mol)
X_1	0.5
X_2	0.5
ν_{d1}	1.0×10^{13} s^{-1}
ν_{d2}	1.0×10^{13} s^{-1}
E_{d1}	75.3 kJ/mol (18.0 kcal/mol)
E_{d2}	96.2 kJ/mol (23.0 kcal/mol)

bulk metal present. It is assumed that the subsurface region is homogeneous and that the adsorbate in the subsurface distributes evenly over the entire region. To account for gradients in the adsorbate concentration in the layers near the surface, additional parameters would be required that can not be measured or estimated *a priori*. A distributed model such as Fick's law is not applicable here since we are only considering diffusion in the topmost atomic layers. The processes occurring during a TPD experiment when both readsorption and subsurface diffusion are important are represented in Figure 4.

Initially, the surface is covered with adsorbate up to some initial coverage θ_0. During heating, the adsorbate will be removed from the surface by both desorption into the gas phase with rate r_d, and by penetration into the subsurface region at a rate r_p. Once the adsorbate desorbs, it either readsorbs, r_a, or is swept out of the reactor by the carrier gas. Any adsorbate that penetrates into the subsurface region can diffuse back to the surface at a rate r_D. A mass balance on the surface region yields:

$$\frac{d\theta}{dt} = nk_a(1-\theta)^n C_G - nk_d\theta^n - k_p\theta(1-\xi) + k_D(1-\theta)\xi \quad (11)$$

The first two terms on the righthand side of Eq. 11 are the rates of adsorption and desorption, respectively. The difference between them equals the net rate of desorption, R_d. The third and fourth terms represent respectively the rate of penetration of adsorbate into the subsurface, and the rate of diffusion from the subsurface back to the surface. The rate of penetration into the subsurface is assumed to be first order in the surface coverage, and first order in the fraction of subsurface sites that are empty. Similarly, the rate of diffusion from the subsurface to the surface is assumed to be first order in the fraction of filled subsurface sites ξ, and first order in the fraction of free surface sites. The rate constants for penetration, k_p, and backdiffusion, k_D, are assumed to follow Arrhenius expressions with constant preexponential factors and activation energies.

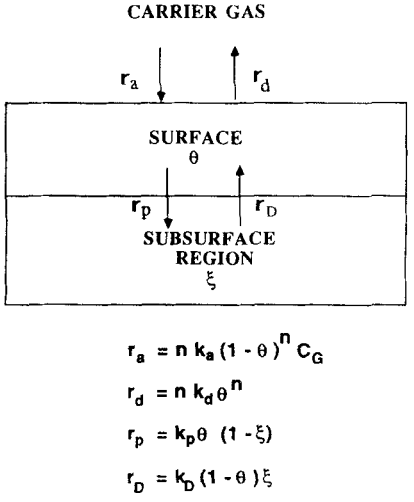


Figure 4. Processes occurring during TPD when both readsorption and subsurface diffusion are important.

The concentration of the adsorbate in the carrier gas when there is only one adsorption site simplifies to

$$C_G = \frac{\frac{N_S}{Q}k_d\theta^n}{1+\frac{N_S}{Q}k_a(1-\theta)^n} \quad (12)$$

A mass balance on the subsurface region yields:

$$\frac{d\xi}{dt} = \frac{1}{M}[k_p\theta(1-\xi) - k_D(1-\theta)\xi] \quad (13)$$

where M is the ratio of the total number of subsurface sites to surface sites ($M = N_B/N_S$). Equations 11 and 13 are equivalent to those used by Davenport et al. (1982) to describe the kinetics of hydrogen solution in transition metals.

In this paper we only consider the case where the adsorbate is not present in the subsurface initially. Therefore, the initial conditions are

$$\text{at} \quad t = 0,\ T = T_0,\ \theta = \theta_0,\ \xi = 0 \quad (14)$$

Equations 7, 11, and 13 were solved simultaneously with a fourth-order Runge-Kutta method for the parameter values listed in Table 2. These values are similar to those used to describe the diffusion of hydrogen in the subsurface of palladium during TPD (Leary et al., 1987a). The parameters were modified slightly in this paper to give better resolution of the peaks.

The results of the simulation are shown in Figure 5. This figure shows that the adsorbate is removed from the surface by

Table 2. Parameter Values Used in Subsurface Diffusion Model

N_S	3.0×10^{-6} mol
m	2.0
n	2.0
M	1.0
S_0	0.005
σ	4.0×10^8 cm^2/mol (4.0×10^4 m^2/mol)
ν_d	1.0×10^{13} s^{-1}
E_d	79.5 kJ/mol (19.0 kcal/mol)
ν_p	1.0×10^6 s^{-1}
E_p	62.8 kJ/mol (15.0 kcal/mol)
ν_D	1.0×10^6 s^{-1}
E_D	58.6 kJ/mol (14.0 kcal/mol)
ξ_0	0.0

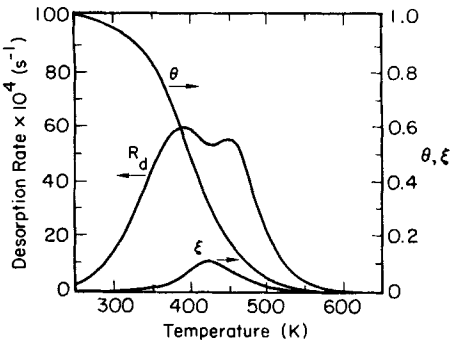


Figure 5. Simulated TPD spectrum using subsurface diffusion model for parameter values in Table 2.
Also shown: changes in surface and subsurface coverages with temperature

both desorption and penetration into the subsurface region. As the surface adsorbate concentration decreases, R_d goes through a maximum and then decreases. When the surface coverage becomes sufficiently small, there is a net diffusion of adsorbate from the subsurace region back to the surface, and the desorption spectrum becomes diffusion-limited. As the temperature rises, the diffusion rate increases since diffusion is an activated process, and R_d also increases. Eventually, as the subsurface adsorbate concentration also decreases, R_d goes through another maximum and decreases, producing a second peak that we refer to as a diffusion peak. Thus Figure 5 clearly shows that subsurface diffusion can produce an extra peak in a TPD spectrum.

It is important to note that subsurface diffusion does not always lead to an extra peak in a TPD spectrum. In order to observe a diffusion peak, the rate of diffusion between the surface and subsurface must be comparable to the net rate of desorption, R_d. This is illustrated by examining the effect of changing the diffusion preexponential factors, as shown in Figure 6. If diffusion is much slower than the net desorption rate, curve *a*, then only one peak is observed in the spectrum: the one due to desorption from the surface. If the diffusion rate is much higher than the net desorption rate, curve *d*, the desorption never becomes limited by the diffusion process, and we again observe only one peak. This peak occurs at a higher temperature than that in curve *a* because diffusion into the subsurface during the temperature ramp decreases the surface coverage. Since the desorption rate is second order in the surface coverage, the net desorption rate is reduced and the peak shifts to higher temperature.

Comparison of Multisite and Subsurface Diffusion Models

We have shown that both the multisite model and the subsurface diffusion model can simulate two peaks in a TPD spectrum. In this section we present a method to distinguish between the two models experimentally.

There are four experimental variables: the initial coverage, the carrier gas flow rate, the heating rate, and the number of surface sites; the last is determined by the amount of catalyst placed in the reactor. From Eqs. 3 and 12 we know that the number of surface sites and the carrier gas flow rate can be combined into one variable, the ratio N_S/Q. This leaves us with only three variables (θ_0, N_S/Q, and β) that can be varied independently. By comparing the changes in the spectrum predicted by each model as these parameters are varied, we can determine for which variables the two models predict different behavior. We can then use this result to distinguish between the two models.

Figure 7 shows the effect of initial coverage on the TPD spectrum simulated by the subsurface diffusion model. Since the desorption rate is second order in the surface coverage and the diffusion rate is first order, the desorption rate decreases with coverage more rapidly than the diffusion rate. Therefore, at low coverages the diffusion rate is much higher than the desorption rate and the spectrum never becomes diffusion-limited. As a result, only one peak is observed in the spectrum. At higher initial coverages the desorption rate becomes comparable to the diffusion rate, and two peaks become resolved. If we compare Figure 7 with the results from the multisite model in Figure 3, we see that the two models predict similar changes in the spectrum as the initial coverage is varied. Therefore, varying the initial coverage will not help to distinguish between the two models.

The next experimental parameter that we can change is the ratio N_S/Q. This is accomplished most easily by varying the carrier gas flow rate Q_0. Figure 8 shows how the two models predict that the spectrum should change as the flow rate is varied. According to the multisite model, Figure 8a, the peaks should shift to lower temperatures and the resolution between the two peaks should improve slightly as the flow rate increases. The reason for this is that an increase in the flow rate causes a

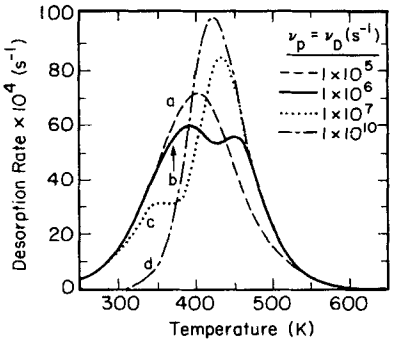


Figure 6. Effect on simulated TPD spectrum of changing values of diffusion preexponential factors in subsurface diffusion model.
Q_0 = 100 cm³/min; θ_0 = 1.0; ξ_0 = 0.0; β = 1.0 K/s

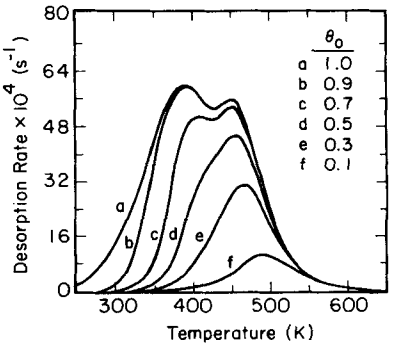


Figure 7. Effect of initial surface coverage on TPD spectrum simulated by subsurface diffusion model.
Q_0 = 100 cm³/min; ξ_0 = 0.0; β = 1.0 K/s

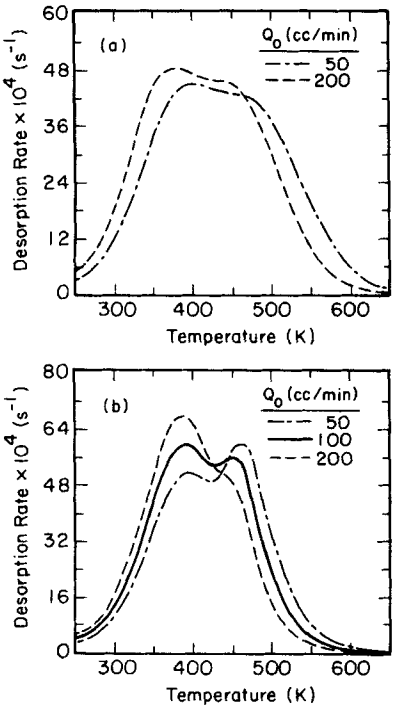


Figure 8. Effect of carrier gas flow rate on TPD spectra simulations.

(a) Multisite model; (b) Subsurface diffusion model
$\theta_0 = 1.0$; $\beta = 1.0$ K/s

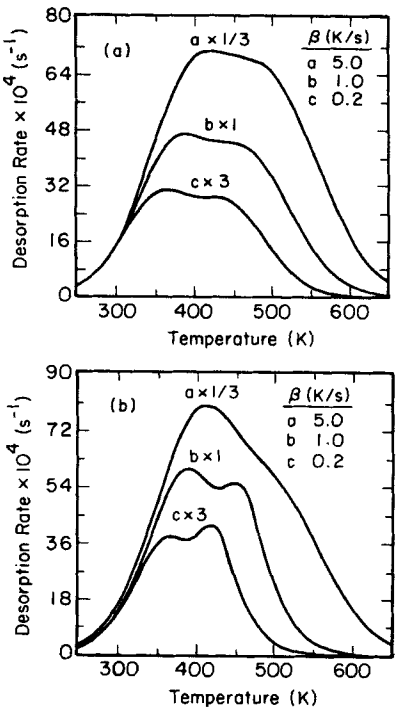


Figure 9. Effect of heating rate on TPD spectra simulations.

(a) Multisite model; (b) Subsurface diffusion model
$\theta_0 = 1.0$; $Q_0 = 100$ cm^3/min

decrease in the gas phase adsorbate concentration, Eq. 3, and this decreases the rate of readsorption. This in turn causes an increase in the net desorption rate and a shift in the peaks to lower temperatures. Figure 8a also shows that if the two peaks are produced by two distinct adsorption sites, the relative sizes of the two peaks do not change significantly as the flow rate is varied. This is in sharp contrast to what is predicted by the subsurface diffusion model, Figure 8b. While an increase in the flow rate causes an increase in the net desorption rate from the surface, the flow rate does not directly affect the diffusion rate. Therefore as the flow rate increases, the desorption rate increases relative to the diffusion rate and less adsorbate diffuses into the subsurface region during heating. This causes a substantial decrease in the size of the diffusion peak relative to the desorption peak. Thus, the two models predict very different behavior as the flow rate is varied. Therefore, by varying the carrier gas flow rate, we can distinguish between the multisite model and the subsurface diffusion model.

A distinction between the two models also can be made from the effect of heating rate on the spectrum, as shown in Figure 9. Figure 9a shows the changes in the spectrum predicted by the multisite model as the heating rate is varied. As the heating rate increases, the peaks shift to higher temperatures but the relative sizes of the two peaks do not change significantly. However, in the subsurface diffusion model the relative sizes of the peaks can change substantially as the heating rate is varied. When E_D is much greater than E_d, the diffusion peak increases in size relative to the desorption peak as the heating rate increases. Conversely, when E_D is much less than E_d, Figure 9b shows that the diffusion peak decreases in size relative to the desorption peak as the heating rate increases.

Thus, by studying the effect of carrier gas flow rate and heating rate on the spectrum, we can distinguish between the multisite model and the subsurface diffusion model experimentally. However, it is important to note that while multiple peaks in TPD spectra are most commonly assigned to multiple adsorption states, there are other models that can account for multiple peaks in a spectrum. Therefore, it is important to be able to distinguish between the subsurface diffusion model and these other models as well. In certain instances lateral interactions between adsorbate molecules can produce additional peaks in a TPD spectrum. Also, if the catalyst has a bimodal pore size distribution, this too could produce two peaks in a spectrum. However, we would expect that in both cases an increase in the carrier gas flow rate would result in improved resolution of the two peaks without any significant change in the relative peak heights, as was the case in the multisite model. Thus, it should be possible to distinguish between the subsurface diffusion model and the other models by measuring the effect of flow rate on the spectrum.

The subsurface diffusion model could also be used to describe spillover of adsorbate from a metal surface onto a support during heating, and then diffusion back to the metal surface when it becomes depleted by the desorption process. As a result it is not possible to distinguish between spillover and subsurface diffusion based on the flow rate and heating rate dependence of the spectrum. Therefore, in cases where spillover may occur, additional experiments are required to distinguish between these possibilities. This is discussed in detail in another paper (Leary et al., 1987a), where we have shown that subsurface diffusion of hydrogen in palladium produces a high-temperature peak in the TPD spectrum of hydrogen on a 9% Pd/SiO_2 catalyst.

Determination of Rate Parameters from TPD Spectra

A major advantage of TPD over chemisorption studies is that it can be used to determine the heat of adsorption on each of the individual adsorption sites instead of obtaining an average over the entire surface. In this section we show how the heat of adsorption is usually measured, and note some precautions that must be taken when deriving quantitative information from TPD spectra. We also show that when a diffusion peak is present in the spectrum, TPD can be used to estimate the activation energy for diffusion from the subsurface to the surface.

In the absence of mass transfer limitations, and assuming equilibrium readsorption, the heat of adsorption, ΔH, on each type of site can be determined from the expression (Rieck and Bell, 1984)

$$\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{\Delta H}{RT_p} + \ln\left[\frac{RnQA\theta_p^{n-1}}{N_S\Delta H(1-\theta_p)^{n+1}}\right] \qquad (15)$$

where T_p is the peak temperature, θ_p is the coverage at the peak temperature, and A is the ratio of the desorption preexponential factor to the adsorption rate constant. If the adsorption is not activated, ΔH is equal to the activation energy for desorption, E_d. Since θ_p does not vary significantly with heating rate (Falconer and Schwarz, 1983), E_d for each site can be determined simply from the slope of a plot of $\ln(\beta/T_p^2)$ vs. $1/T_p$ for each peak. However, when this method is applied to spectra containing multiple peaks, care must be taken in determining the desorption activation energies.

Figure 9a shows the effect of heating rate on the TPD spectrum from a surface containing two sites. As the heating rate increases, the peaks shift to higher temperatures as expected from Eq. 15, and the overlap between the peaks increases. The overlap causes the low-temperature peak to be shifted upward in temperature, and the high-temperature peak to be shifted downward in temperature. Since the overlap between the peaks increases at higher heating rates, the low-temperature peak is shifted upward in temperature more than it would have been in the absence of the high-temperature peak. Conversely, the high-temperature peak is not shifted as much with temperature as it would be if the low-temperature peak were not present. This is shown more clearly in Figure 10, where the net desorption rates from the individual sites are plotted as well as R_d from the entire surface. Figures 10a and 10b show that the overlap of the two peaks causes the low temperature peak to be shifted upward in temperature by 14 K when β = 0.2 K/s, and by 27 K when β = 5.0 K/s. The increased overlap at higher heating rates causes the shift in the low-temperature peak with heating rate to be overestimated by 13 K. Therefore, when E_d is calculated from shift in the peak temperature with heating rate, it is underestimated. From the spectra shown in Figure 9a, we calculate E_{d1} = 66.9 kJ/mol (16 kcal/mol), which is 11% lower than the value of 75.3 kJ/mol (18 kcal/mol) input to the model.

Figures 10a and 10b also show that the high-temperature peak is shifted downward in temperature by 26.5 K when β = 0.2 K/s. When β = 5.0 K/s, the high-temperature peak is no longer resolved clearly, and appears as a shoulder on the low-temperature peak. If the inflection point immediately to the left of the high-temperature shoulder is taken as an estimate of the peak temperature, a downward shift of 38 K is obtained. Thus,

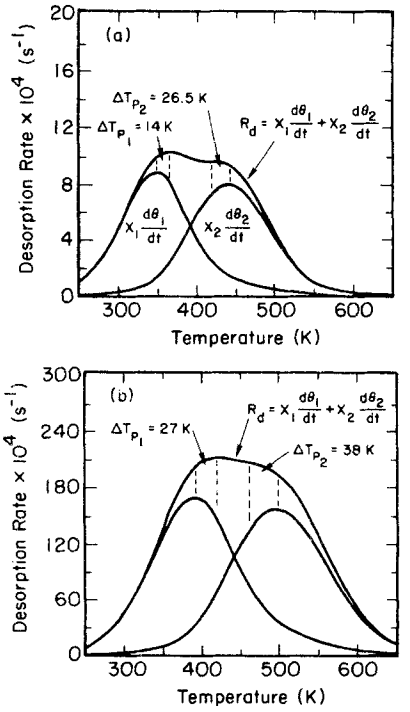


Figure 10. TPD spectra simulated by multisite model at two heating rates.

(a) 0.2 K/s; (b) 5.0 K/s

Net desorption rates from individual sites, as well as net desorption rate from entire surface are shown

Also shown: shifts in peak temperatures caused by overlap between peaks

the shift with peak temperature is underestimated by 11.5 K, causing E_d to be overestimated. From the spectra in Figure 9a, we calculate E_{d2} = 109.2 kJ/mol (26.1 kcal/mol), which is 13% higher than the value of 96.2 kJ/mol (23 kcal/mol) input to the model. The error in the desorption energy of the high binding energy site caused by peak overlap can be avoided by performing the heating rate variation experiment at an initial coverage for which only this site is filled.

In cases where a diffusion peak appears in the TPD spectrum, a plot of $\ln(\beta/T_p^2)$ vs. $1/T_p$ can be used to estimate the activation energy for diffusion from the subsurface to the surface. This is because the net desorption rate becomes diffusion-limited. However, since net diffusion of adsorbate from the subsurface to the surface does not occur until the surface is substantially depleted of adsorbate by desorption, the location of the diffusion peak is in part determined by the location of the desorption peak. Therefore, the shift in the diffusion peak temperature with heating rate contains two contributions: the shift due to the activated nature of the diffusion process, and the shift due to the change in the desorption peak temperature. As a result, the measured activation energy will lie between the values for the diffusion activation energy E_D, and the desorption activation energy E_d.

Our modeling studies show that if the relative size of the two peaks and the resolution between them does not change substantially as the heating rate is varied, then the activation energy determined corresponds closely to the value of E_D. To meet this requirement, a smaller range of heating rates must be used, and this makes it very important to determine the peak temperatures

accurately. If the relative sizes of the two peaks or the resolution between them changes substantially, then the measured activation energy will lie closer to the value of E_d. This is the case in Figure 9b from which an activation energy of 69.0 kJ/mol (16.5 kcal/mol) is calculated for the diffusion peak. This value is approximately equidistant between the values of E_d = 79.5 kJ/mol (19 kcal/mol) and E_D = 58.6 kJ/mol (14 kcal/mol). Moreover, it is important to note that mass transfer limitations also can cause errors in measuring activation energies from TPD spectra. As discussed by Demmin and Gorte (1984), it is often very difficult to eliminate the effects of mass transfer limitations. Thus, care must be taken when estimating E_D from TPD spectra.

Summary

Two models have been presented that can account for two peaks in a TPD spectrum: a multisite model and a subsurface diffusion model. The multisite model assumes that the two peaks are produced by two distinct types of adsorption sites on the catalyst surface which differ in binding energy. The subsurface diffusion model assumes that the high-temperature peak is produced by adsorbate that diffuses into the subsurface of the material during heating and then back to the surface when it becomes depleted by the desorption process. We have shown that it is possible to distinguish between these two models experimentally by measuring the effects of flow rate and heating rate on the spectrum. If the two peaks are produced by two sites, then changing the carrier gas flow rate of heating rate does not affect the relative heights of the two peaks significantly. However, if the high-temperature peak is a diffusion peak, then the size of this peak decreases markedly relative to the desorption peak as the flow rate increases. The relative heights of the diffusion and desorption peaks also can change significantly as the heating rate is varied.

We also have shown that significant errors can be made in determining desorption activation energies from the individual sites from the shifts in peak temperatures with heating rate. The decrease in resolution of the peaks as the heating rate increases can cause the activation energy for desorption from the low binding energy sites to be underestimated, and the activation energy for the high binding energy sites to be overestimated. The activation energy for desorption from the high energy sites can be determined accurately by working at initial coverages where only these sites are filled.

Finally, we have shown that if a diffusion peak is present in the spectrum, the shift in its peak temperature with heating rate can be used to estimate the activation energy for diffusion from the subsurface to the surface.

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Notation

A = ratio of preexponential factor for desorption to adsorption rate constant, mol/cm^3
C_G = gas phase adsorbate concentration, mol/cm^3
E_d = activation energy for desorption, kJ/mol
E_{di} = activation energy for desorption from site i, kJ/mol
E_D = activation energy for diffusion from subsurface to surface, kJ/mol
E_p = activation energy for penetration of adsorbate into subsurface region, kJ/mol
ΔH = heat of adsorption, kJ/mol
k_a = rate constant for adsorption, cm^3/mol · s
k_d = rate constant for desorption, s^{-1}
k_D = rate constant for diffusion from subsurface to surface, s^{-1}
k_p = rate constant for penetration of adsorbate into subsurface region, s^{-1}
m = molecular weight of adsorbate
M = ratio of total number of subsurface sites to surface sites, $M = N_B/N_S$
n = desorption order
N_B = total number of subsurface sites, mol
N_S = total number of surface sites, mol
Q = temperature-dependent carrier gas flow rate, cm^3/min
Q_0 = carrier gas flow rate at STP, cm^3/min
r_a = readsorption rate, s^{-1}
r_d = desorption rate, s^{-1}
r_D = rate of diffusion from subsurface to surface, s^{-1}
r_p = rate of penetration of adsorbate into subsurface region, s^{-1}
R = gas constant
R_d = net desorption rate, $R_d = r_d - r_a$
S_0 = sticking coefficient
t = time, s
T = temperature, K
T_p = peak temperature, K
X_1 = fraction of sites that are type 1
X_2 = fraction of sites that are type 2

Greek letters

β = heating rate, K/s
σ = surface area occupied by one mole of adsorption sites, cm^2/mol
θ = surface coverage of adsorbate in subsurface diffusion model
θ_0 = initial surface coverage in subsurface diffusion model
θ_1 = fraction of type 1 sites filled in multisite model
$\theta_1^{(0)}$ = initial coverage of type 1 sites
θ_2 = fraction of type 2 sites filled in multisite model
$\theta_2^{(0)}$ = initial coverage of type 2 sites
θ_T = total surface coverage in multisite model
$\theta_T^{(0)}$ = initial total surface coverage in multisite model
ξ = subsurface coverage of adsorbate
υ_d = preexponential factor for desorption, s^{-1}
υ_{di} = preexponential factor for desorption from site i, s^{-1}
υ_D = preexponential factor for diffusion from subsurface to surface, s^{-1}
υ_p = preexponential factor for penetration of adsorbate into subsurface region, s^{-1}

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