

Saturation Effects in Temperature-Programmed Desorption Spectra Obtained from Porous Catalysts

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INTRODUCTION

Recently there has been renewed interest in applying temperature-programmed desorption techniques to porous catalysts (1-9). Although not explicitly stated by many authors, there are several potential advantages in using TPD techniques to study adsorption energetics, as opposed to the conventional practice of measuring adsorption isotherms at various temperatures. These include:

- The ability to collect data rapidly.
- Elimination of the need for a direct measurement of adsorbate coverage.
- Better resolution of energetically similar adsorption states, and of adsorbate interaction energies.

The principle complication of the TPD technique when applied to porous catalysts is that readsorption effects can lead to a fundamental change in the information content of the TPD spectrum. The desorption step is no longer the rate-limiting process, and the measured flux of molecules leaving the sample is instead determined by *the rate of diffusion of molecules out of the catalyst pores, as modified by adsorption on the pore walls*. This situation will prevail in typical experimental configurations unless a significant activation barrier for readsorption exists. The difference in rate-determining process for porous TPD experiments has been stressed by recent authors (8, 9), but has not been fully appreciated by all workers in the field.

For the case of diffusion-limited TPD spectra, an analytic expression relating q_{st} ,

the isosteric heat of adsorption, to T_m , the peak temperature, was originally developed by Cvetanovic and Amenomiya (1):

$$\frac{q_{st}}{RT_m} = \ln\left(\frac{\pi^2 a D_0 T_m^{2+\alpha}}{8 l^2 \beta K_0}\right) - \ln\left(\frac{q_{st}}{R}\right), \quad (1)$$

where a and l are the pore radius and pore length that determine the diffusion characteristics of the catalyst sample, $D_0 T^\alpha$ is the diffusion coefficient, β is the heating rate, and K_0 is the preexponential factor of the adsorption equilibrium constant. This equation was based on a one-dimensional diffusion model and the assumption of a linear adsorption isotherm,

$$n = K_{eq} c_g, \quad (2)$$

where n is the surface concentration of adsorbed molecules, c_g is the concentration of molecules in the gas phase, and the adsorption equilibrium constant, K_{eq} , is assumed to have the form

$$K_{eq} = K_0 \exp(q_{st}/RT). \quad (3)$$

Unfortunately, many adsorption systems are better described by a Langmuir isotherm, which reflects the fact that a finite concentration of adsorption sites, n_{max} , exists on the surface. For these systems, Eq. (2) should be replaced by

$$\theta = K_{eq} c_g / (1 + K_{eq} c_g), \quad (4)$$

where $\theta = n/n_{max}$ is the fractional coverage of adsorbate. Because of saturation effects associated with Eq. (4), one expects the peak temperature and coverage dependence for an adsorbate that obeys

Langmuir adsorption to be different from that predicted by Eq. (1).

In this paper we present an analysis of the TPD process in a catalyst pore for an adsorbate which exhibits Langmuir isotherm behavior. An expression is derived which relates T_m to the *adsorption energy*, U_{ads} , and the initial coverage, θ_0 . We show that, as a result of saturation effects, T_m shifts to lower temperatures with increasing θ_0 ; the shift is relatively small but can be easily included when interpreting TPD data.

THEORY

The analytical approach follows that developed by Cvetanovic and Amenomiya (1). We model the TPD process as gas-phase diffusion of desorbed species out of a uniform cylindrical pore of radius a and length l . The open end of the pore ($x = 0$) empties into an external volume that is well mixed and evacuated at a constant volumetric flow rate. At the initial temperature all adsorbate molecules are irreversibly bound on the pore wall. As the temperature is increased, molecules desorb, diffuse out of the pore while undergoing occasional readsorption, and finally are pumped out of the external volume. The model is applicable to the experimental configuration consisting of a catalyst disk suspended in an evacuated cell, as used in our laboratory (10).

For diffusion to be the rate-limiting process, two criteria must be satisfied (9). First, local equilibrium must exist between gas-phase and adsorbed species at each position within the pore. This will occur if the relaxation time for achieving equilibrium between gas-phase and adsorbed species in a closed pore ($\tau_{eq} = a/2k_a$, where k_a is the rate constant for adsorption) is much shorter than the relaxation time for diffusion of gas-phase molecules within the pore ($\tau_{diff} = l^2/D$):

$$\frac{\tau_{eq}}{\tau_{diff}} = \frac{aD}{2k_a l^2} \ll 1. \quad (5)$$

This is essentially the criterion VI derived by Gorte (9). If we make the reasonable estimates that $D = (2/3)av$ for Knudsen diffusion and $k_a = (1/4)Sv$, where v is the average velocity of gas molecules and S is the sticking coefficient for adsorption, we can write a simplified criterion for the existence of local adsorption equilibrium,

$$\left(\frac{a}{l}\right)^2 \ll S. \quad (6)$$

This result has the form expected from a random walk analysis of molecular diffusion out of a pore.

The second criterion is that the concentration of gas-phase molecules external to the catalyst pore, c_e , be negligible compared to the maximum concentration inside the pore; i.e., that all of the concentration drop occurs within the catalyst sample. This is satisfied if

$$\frac{Fl}{2A_e D} \gg 1, \quad (7)$$

where F is the volumetric flow rate out of the sample cell (cm³/sec) and A_e is the superficial area of the catalyst sample. This corresponds to criterion III listed by Gorte (9), and represents the stipulation that the volumetric flow out of the sample cell be fast enough to prevent a significant buildup of c_e due to the adsorbate flux diffusing out of the catalyst sample.

The conservation equation which governs adsorbate diffusion out of the pore is

$$\frac{\partial}{\partial t} \left(c_g + \frac{2}{a}n \right) = D \frac{\partial^2 c_g}{\partial x^2}, \quad (8)$$

where D is assumed to be independent of position and concentration. In a properly designed experiment, the relaxation time for diffusion (l^2/D) will be much shorter than the duration of the experiment (cf. criteria IV in Ref. (9)). Under this circumstance, dimensional analysis shows that

$$\frac{\partial c_g}{\partial t} \ll D \frac{\partial^2 c_g}{\partial x^2}. \quad (9)$$

Physically, this means that essentially all of the adsorbate remaining in the pore at a given time is present in the adsorbed state. Analytically, this means that Eq. (8) can be simplified to

$$\frac{\partial}{\partial t} \left(\frac{2n}{a} \right) = D \frac{\partial^2 c_g}{\partial x^2}. \quad (10)$$

Provided that local equilibrium exists between gas-phase and adsorbed species, Eq. (4) can be substituted into Eq. (10) to eliminate c_g . The resulting conservation equation contains only a single dependent variable, $\theta(x, t)$. Since K_{eq} is assumed to be independent of θ or x for a Langmuir isotherm, the equation can finally be written in dimensionless form for solution,

$$\frac{\partial \theta}{\partial \tau} = \frac{\partial^2}{\partial \eta^2} \left(\frac{\theta}{1 - \theta} \right), \quad (11)$$

where $\eta = x/l$, and all of the system-specific parameters are contained in the dimensionless time variable, τ . This "pseudotime" variable is *differentially* related to real time by

$$d\tau = \frac{aD_0 T^{(m+\alpha)}}{2l^2 K_0} \exp\left(\frac{-U_{ads}}{RT}\right) dt. \quad (12)$$

The exponent m is included in Eq. (12) to account for the exact form of the temperature dependence of K_{eq} predicted by statistical mechanics (11):

$$K_{eq} = K_0 T^{-m} \exp(U_{ads}/RT). \quad (13)$$

The isosteric heat of adsorption is related to U_{ads} and m :

$$\begin{aligned} q_{st} &= -RT^2 \frac{\partial \ln(K_{eq})}{\partial T} \\ &= U_{ads} + mRT. \end{aligned} \quad (14)$$

For the solution to Eq. (11) described here, the usual boundary, initial, and transient conditions are assumed:

$$\theta = 0 \quad (\eta = 0), \quad (15)$$

$$\frac{\partial \theta}{\partial \eta} = 0 \quad (\eta = 1), \quad (16)$$

$$\theta = \theta_0 \quad (0 < \eta \leq 1; t > 0), \quad (17)$$

$$T = T_0 + \beta t \quad (t > 0), \quad (18)$$

where β is the sample heating rate.

The desorption rate in real time, $I(t)$, is described by

$$I(t) = (dH/d\tau)(d\tau/dt), \quad (19)$$

where H is the amount of adsorbate remaining in the pore at time τ :

$$H(\tau) = (1/\theta_0) \int_0^1 \theta(\eta, \tau) d\eta. \quad (20)$$

The peak temperature, T_m , is found by locating the maximum of Eq. (17). After substituting Eq. (12) for $(d\tau/dt)$, differentiating, and setting the result equal to zero, one obtains

$$\begin{aligned} \frac{U_{ads}}{RT_m^2} - \frac{(m + \alpha)}{T_m} &= \left(-\frac{H''}{H'} \right)_{T_m} \times \\ &\frac{aD_0 T_m^{(m+\alpha)}}{2l^2 \beta K_0} \exp\left(\frac{-U_{ads}}{RT_m}\right), \end{aligned} \quad (21)$$

where $H'' = d^2H/d\tau^2$ and $H' = dH/d\tau$.

Exact solution of Eq. (21) still requires numerical calculation of the complete TPD spectrum in order to evaluate $(-H''/H')_{T_m}$. However, in the course of calculating the simulated spectra discussed below, we observed that the latter factor can be described to $\pm 10\%$ by the expression

$$\left(-\frac{H''}{H'} \right)_{T_m} = \frac{\pi^2/4}{(1 - \theta_0/2)^2}. \quad (22)$$

A second simplification of similar accuracy is the neglect of the second term on the lhs of Eq. (21). This follows from the observation that U_{ads}/RT_m is typically an order of magnitude larger than the temperature exponents, $(m + \alpha)$.

The final expression for relating U_{ads} and T_m is then

$$\frac{U_{ads}}{RT_m} = \ln\left(\frac{\pi^2 a D_0 T_m^{(2+m+\alpha)}}{8l^2 \beta K_0 (1 - \theta_0/2)^2}\right) - \ln\left(\frac{U_{ads}}{R}\right). \quad (23)$$

Inspection of this equation shows that for species which exhibit a Langmuir adsorption isotherm, the peak temperature will shift as a function of initial coverage. The

maximum magnitude of this shift will be $\sim 5\%$, relative to T_m , as the initial coverage approaches saturation.

DISCUSSION

In the following paragraphs we wish to illustrate the application of the equations developed above, and to discuss the assumptions and limitations contained in the model.

For experimental conditions where the TPD process is diffusion limited (cf. Eqs. (5) and (7)), the desorption process can be best thought of as the diffusional emptying of a finite porous media, modified by adsorption of the diffusing species. The well-resolved maximum in the desorption flux that is characteristic of TPD spectra arises from the highly nonlinear temperature dependence of the adsorption equilibrium constant. At low temperatures, transport out of the sample occurs slowly because molecules spend most of their time in the adsorbed state. As the temperature is increased, the molecules spend more time in the gas phase, and diffusion out of the sample occurs at an ever-increasing rate.

This process is illustrated in Figs. 1–3. In Fig. 1 we show a series of concentration profiles at successive stages of pore empty-

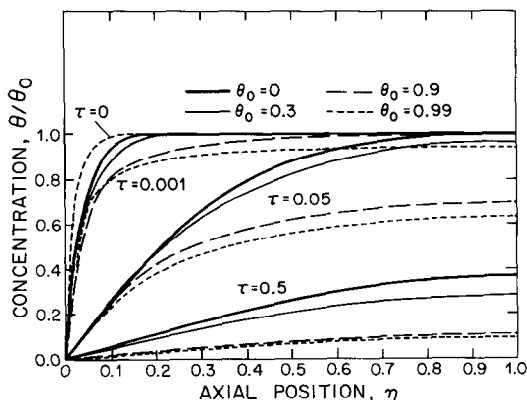


FIG. 1. Concentration profiles within catalyst pore at successive stages of development for various initial coverages. (Lim $\theta_0 \rightarrow 0$ corresponds to linear adsorption isotherm.)

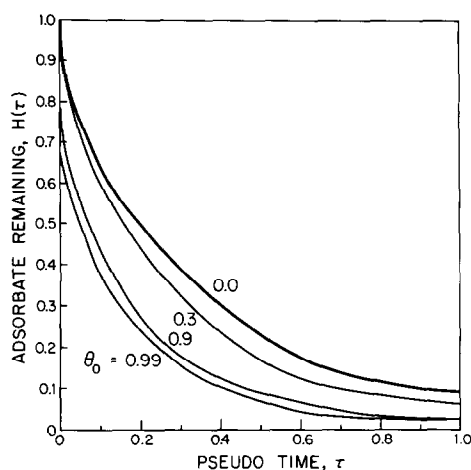


FIG. 2. Amount of adsorbate remaining in catalyst pore as a function of time for various initial coverages.

ing ($\tau = 0.001, 0.05, \text{ and } 0.5$) obtained by numerical integration of Eq. (11). For each value of τ , we show profiles that result from various values of initial coverage ($\theta_0 = 0.99, 0.9, \text{ and } 0.3$, and $\lim \theta_0 \rightarrow 0$). Each profile is normalized by the corresponding value of θ_0 .

The influence of the Langmuir adsorption isotherm can be seen by comparing concentration profiles at each value of τ for different initial coverages. The profiles decay more rapidly for higher initial coverages, since the higher fraction of occupied sites means that diffusing molecules are less likely to be “restrained” by readsorption. This effect is also apparent in Crank’s solution for diffusion of Langmuir adsorbates in cylindrical pores (12). The saturation-induced enhancement of the pore emptying rate is more pronounced at short times. As shown below, this leads to an increase in the desorption flux on the leading edge of the TPD spectra.

In Fig. 2 we show the amount of adsorbate remaining, $H(\tau)$, as a function of τ for each of the initial concentrations shown in Fig. 1. These curves show more clearly that the pore empties more rapidly for larger initial coverages. For $\theta_0 = 0.0$, half of the initial adsorbate has left the pore by $\tau_{1/2} = 0.19$, while for $\theta_0 = 0.99$, the time required

to half-empty the pore decreases to $\tau_{1/2} = 0.05$.

The development to this point is completely general for any adsorbate that exhibits a Langmuir isotherm. The function $H(\tau)$ and its derivatives depend only on the initial coverage. The influence of *all other system-specific parameters* (e.g., a , l , D , β , K_0 , and U_{ads}) is contained in the factor $(d\tau/dt)$ in Eq. (19).

In Fig. 3 we show a set of calculated TPD spectra that illustrate the effect of initial coverage on T_m . The solid curves were obtained by solving Eq. (19), based on $H(\tau)$ for each initial coverage shown in Fig. 2 and the pseudotime transformation, $\tau(t)$, obtained by integrating Eq. (12). We have selected system parameters representative of CO adsorption on ZnO (Kadox 25): $a = 10^{-5}$ cm, $l = 0.05$ cm, $D = 0.1$ cm²/sec, $K_0 = 1.8 \times 10^{-8}$ cm-K^{5/2}, $m = 5/2$, $U_{\text{ads}} = 12.2$ kcal/mole, and $\beta = 0.15$ K/sec (13).

The dashed curve in Fig. 3 shows the spectrum that would be obtained if readsorption is completely neglected; i.e., the spectrum obtained for first-order desorption from a flat surface into a vacuum:

$$\frac{d\theta}{dt} = -v_0 \exp(-U_{\text{ads}}/RT)\theta, \quad (24)$$

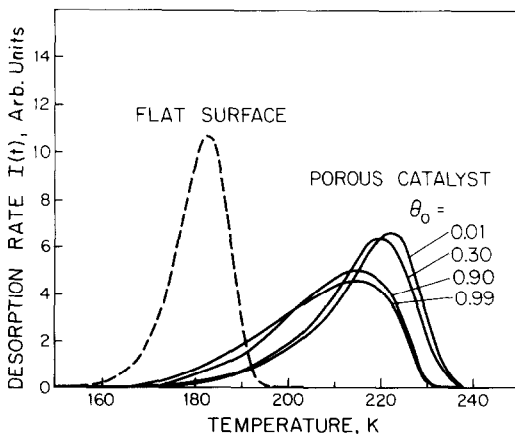


Fig. 3. Calculated TPD spectra based on parameters for CO desorbing from porous ZnO (see text). Solid curves: spectra for various initial coverages. Dashed curve: spectrum for desorption from flat surface into a vacuum (negligible readsorption).

assuming $U_{\text{ads}} = 12.2$ kcal/mole and $v_0 = 10^{13}$ sec⁻¹. All curves are normalized to contain equal areas.

Comparison of the solid and dashed curves shows that for a particular value of U_{ads} , desorption from porous catalysts results in a higher value of T_m than does desorption from a plane surface. This point has been stressed by previous authors (8, 9). Examination of the solid curves shows that, because of saturation effects associated with the Langmuir isotherm, T_m shifts to lower values as the initial coverage is increased. The peak temperature is described quite well (± 1 K) by Eq. (23), and decreases from $T_m = 222$ K for $\theta_0 = 0$ to $T_m = 213$ K for $\theta_0 = 0.99$.

Several comments should be made regarding the applicability of Eq. (23). It has been shown previously (1) that a factor of $(1 - \theta_m)^2$, where θ_0 is the coverage remaining at T_m , will account for saturation effects in the case of flow-limited TPD experiments, where concentration gradients within the pore are negligible. Our present results based on the calculated spectra in Fig. 3 show that a factor of $(1 - \theta_0/2)^2$ in Eq. (23) will describe the temperature shift quite accurately. We have also confirmed the accuracy of Eq. (23) by analyzing the saturation-induced shift in the calculated spectra for CO on supported Pt that are analyzed by Herz (8) and Gorte (9). The magnitude of the coverage-induced shift between $\theta_0 = 0$ and $\theta_0 = 1$ is 4–5% ($= \Delta T_m/T_m$), which is well above the resolution limit for porous TPD experiments (11, 13).

We note that it is unlikely that an experimenter would use the coverage-induced shift to measure n_{max} , since this can be done more easily by observing the saturation limit during uptake measurements. Instead, Eq. (23) is best used to correct for saturation effects with Langmuir adsorbates when attempting to analyze coverage-dependent shifts in T_m that are caused by other effects (e.g., adsorbate interactions, see below).

The assumptions involved in developing

Eq. (23) should also be examined. The use of a concentration-independent diffusion coefficient is not unreasonable based on the Knudsen model for free molecular diffusion in evacuated pores. Discussions of concentration-dependent diffusion coefficients usually involve nonlinear adsorption isotherms that have been incorporated directly into an effective diffusivity. In contrast, in this work the coverage dependence of the Langmuir isotherm is kept separate from the diffusion coefficient (cf. Eq. (10)).

Values for the pore dimensions a and l should be chosen that are representative of the diffusional characteristics of the sample. Typically, a is defined by (14)

$$a = 2V_g/S_g, \quad (25)$$

where V_g and S_g are the specific void volume and surface area of the catalyst. The length l is chosen as the half-thickness of the sample. Additional work is needed to determine the accuracy of these definitions for systems with strongly connected pore networks or bimodal pore size distributions.

We also assume that the initial adsorbate concentration is uniform throughout the pore. Experimentally, a uniform distribution can be achieved trivially for saturation coverage. To achieve a uniform initial distribution at less than saturation coverage, care is needed in the dosing procedure. The most reliable procedure is to start with the sample at a high enough temperature that adsorption is reversible, then cool the sample in the presence of only enough gas to produce the desired adsorbate coverage (13).

The principal limitation of the present work is the assumption that K_{eq} is independent of coverage. This permits use of the pseudotime transformation (Eq. (12)), which will work for any adsorption isotherm of the form

$$c_g = F(t)G(\theta). \quad (26)$$

For $G(\theta) \neq \theta/(1 - \theta)$, Eq. (11) would have to be modified to reflect the specific form of

$G(\theta)$, and the function $H(\tau)$ and its derivatives would need to be recalculated. Solutions for selected forms of $G(\theta)$ are contained in Crank's monograph (12).

Unfortunately, physically realistic descriptions of adsorption usually include a coverage-dependent U_{ads} :

$$U_{ads}(\theta) = U_{ads}^0 + \gamma\theta + 0(\theta^2), \quad (27)$$

where the coefficient γ reflects the magnitude of adsorbate interactions. Alternatively, the adsorption sites may be characterized by a range of adsorption energies. In either case the isotherm cannot be written exactly in the form given by Eq. (26), and the pseudotime transformation (Eq. (11)) cannot be used. Thus the influence of coverage-dependent adsorption energies is beyond the scope of the present work. Some numerical simulations have been reported in (3), which indicate that the coverage-induced shift in T_m due to adsorbate interactions as described by Eq. (27) can be represented approximately by

$$\Delta T_m/T_m \cong (0.8) \frac{\gamma\theta_0}{U_{ads}^0}. \quad (28)$$

Additional analytical work is needed to confirm and/or improve this empirical result.

SUMMARY

For temperature-programmed desorption from porous catalysts where the rate-limiting process is diffusion of gas-phase molecules in local equilibrium with the adsorbed phase (i.e., Eqs. (5) and (7) satisfied), the presence of saturation effects in the adsorption isotherm produces a negative shift in T_m that depends on the initial coverage. The maximum size of this shift for an initially saturated surface is $\sim 5\%$ of T_m . A quantitative prediction of this saturation-induced shift is given by Eq. (23), which can be used to evaluate U_{ads} directly from T_m , provided that θ_0 and the remaining adsorbate-cata-

lyst parameters are known (i.e., a , l , D , K_0 , and β).

NOMENCLATURE

a	pore radius (cm)
A_c	superficial area of sample (cm ²)
c_e	gas-phase concentration external to pore (molecule/cm ³)
c_g	gas-phase concentration within pore (molecule/cm ³)
F	evacuation rate of sample cell (cm ³ /sec)
H	amount of adsorbate remaining in pore (-)
ΔH_{ads}	heat of adsorption (kcal/mole)
k_a	adsorption rate constant (cm/sec)
K_{eq}	adsorption equilibrium constant (cm ³ /molecule)
K_0	temperature-independent coefficient of adsorption preexponential factor (cm-K ^m)
l	half-thickness of sample (cm)
m	temperature exponent for K_0 (-)
n	adsorbate concentration (molecules/cm ²)
q_{st}	isosteric heat of adsorption (kcal/mole)
R	gas constant (0.001987 kcal/mole-K)
S	sticking coefficient (-)
S_g	specific surface area (cm ² /g)
t	real time (sec)
T	temperature (K)
T_m	peak temperature (K)
U_{ads}	energy of adsorption (kcal/mole)
v	molecular speed (cm/sec)
V_g	specific void volume (cm ³ /g)
α	temperature exponent in diffusion coefficient
β	heating rate (K/sec)
γ	adsorbate interaction coefficient (kcal/mole)
D	diffusion coefficient (cm ² /sec)
η	dimensionless length (-)
θ	fractional coverage (-)
τ	pseudotime (-)

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