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Temperature-Programmed Desorption from Porous Catalysts: Shape Index Analysis

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The shape index S of an individual temperature-programmed desorption (TPD) peak is defined as the ratio of slope magnitudes at the two inflection points, an experimental quantity easily determined for any single, reasonably isolated peak. Here we present analyses which indicate that for initial site coverages near unity, a measurement of S can discriminate between four important cases: (1) First-order desorption with no readsorption. (2) First-order desorption with equilibrium readsorption. (3) Second-order desorption with no readsorption. (4) Second-order desorption with equilibrium readsorption. Guidelines for reaction order determination with intermediate degrees of readsorption arise naturally. Comparison of theory and experimental data is encouraging. A criterion to assure that TPD results are free of internal diffusional disguise is suggested; time delay and dispersion-induced sample errors are discussed and shown to be negligible.

INTRODUCTION

In a typical temperature-programmed desorption (TPD) experiment involving a porous catalyst, the solid sample is contacted with an adsorbing gas for an appropriate length of time at a modest or ambient temperature. Subsequently, an inert, steady purging gas flow is established through the small packed bed holding the catalyst. A programmed temperature schedule is initiated, typically linear in time t: $T(t) = T_0 + \beta t$. The effluent gas concentration of desorbed material is then measured and recorded as a function of temperature (time).

Temperature-programmed desorption spectra have been analyzed in the literature for both first- and second-order desorption, with and without the influence of readsorption (*1*, *4*). Parameters which can be easily determined from a single peak are indicated in Figs. 1a, b, and c. These are the temperature at maximum desorption rate, T_m, and the associated site coverage, θ_m (Fig. 1a), the peak width, ΔT (Fig. 1b), and the largest magnitudes of the peak slopes, $d/dT(d\theta/dT)$, corresponding to the two inflection points at T_1 and T_2 (Fig. 1c).

In the following sections we first briefly review analyses using T_m and θ_m (Fig. 1a), and note the level of effort and time required to deduce desorption reaction orders and the presence or absence of readsorption. A subsequent section presents a peak shape analysis of four pertinent cases and establishes how a single peak may be analyzed from its inflection point slopes (Fig. 1c) to give, in a single measurement, a resolution among these four common cases. Three brief final sections treat (i) cases of intermediate degrees of readsorption, (ii) development of a criterion to ensure lack of diffusional disguises during desorption, and (iii) the influence of errors due to time delays and peak dispersion.

TPD ANALYSIS: PEAK TEMPERATURE VARIATIONS

The following convenient terminology is used throughout this paper:

T, T_0	Current and initial temperatures
β	(Linear) rate of temperature rise

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ν_m	Sites (of a given kind)/cm^3 catalyst
k_a, k_d	Adsorption and desorption rate constants (first or second order, as appropriate)
C	Gas phase concentration of desorbing species
A, E	Preexponential factor and activation energy for associated rate constant, k
F	Gas flow rate
A', E'	Preexponential and heat of adsorption for associated equilibrium constant, K

A linear temperature program,

$$T(t) = T_0 + \beta t \tag{1}$$

is customarily established. Instantaneous mass balances are written on the surface phase (*1*),

$$-\nu_m \frac{\partial\theta}{\partial t} = \nu_m k_d \theta^n - \nu_m k_a C(1-\theta)^n \tag{2}$$

(net desorption rate) = (desorption) − (readsorption)

and on the flowing gas phase,

$$FC - F(O) = \nu_m V_c k_d \theta^n - \nu_m V_c k_a C(1-\theta)^n. \tag{3}$$

(exit) − (inflow) = (desorption) − (readsorption)

The concentration (eventually detected) in the gas phase, C, is seen from Eq. (3) to be the following:

$$C(t) = \frac{\nu_m V_c k_d \theta^n}{F + \nu_m V_c k_a (1-\theta)^n}. \tag{4}$$

Equation (4) has been considered under two limiting circumstances, namely, negligible readsorption ($F \gg \nu_m V_c k_a (1-\theta)^n$) and equilibrated readsorption ($F \ll \nu_m V_c k_a (1-\theta)^n$). Evaluation of T_m using Eq. (2) and the limiting forms of (4) when T varies according to Eq. (1) yields the four following relations:

(A) *First-Order Desorption, Negligible Readsorption* (*1*)

$$2 \ln T_m - \ln \beta = \frac{E}{RT_m} + \ln \frac{E}{AR} \tag{5}$$

(B) *First-Order Desorption, Equilibrated Readsorption* (*1, 2*)

$$2 \ln T_m - \ln \beta = \frac{E'}{RT_m} + \ln \frac{E'}{A'R} + \ln \frac{(1-\theta_m)^2 \nu_m V_c}{F} \tag{6}$$

(C) *Second-Order Desorption, Negligible Readsorption* (*1*)

$$2 \ln T_m - \ln \beta = \frac{E}{RT_m} + \ln \frac{E}{AR} - \ln 2\theta_m \tag{7}$$

(D) *Second-Order Desorption, Equilibrated Readsorption* (*2*)

$$2 \ln T_m - \ln \beta = \frac{E'}{RT_m} + \ln \frac{E'}{A'R} + \ln \frac{V_c \nu_m (1-\theta_m)^3}{2F\theta_m}. \tag{8}$$

In assessing which case is appropriate to a given peak, θ_m can be calculated from Fig. 1 or from the often-used approximation, $\theta_m \sim \theta_0/2$ (*1*). Determination of desorption reaction order from porous catalysts requires experiments at various θ_m (or various initial coverages θ_0) (to distinguish between A and Cases B–D) and various flow rates F (to separate Cases B and D from C). The slow heating rates typical of TPD experiments imply considerable time needed to complete a set of such essays. Also, unless θ_m is varied far from $\theta_m \sim 0.5$,

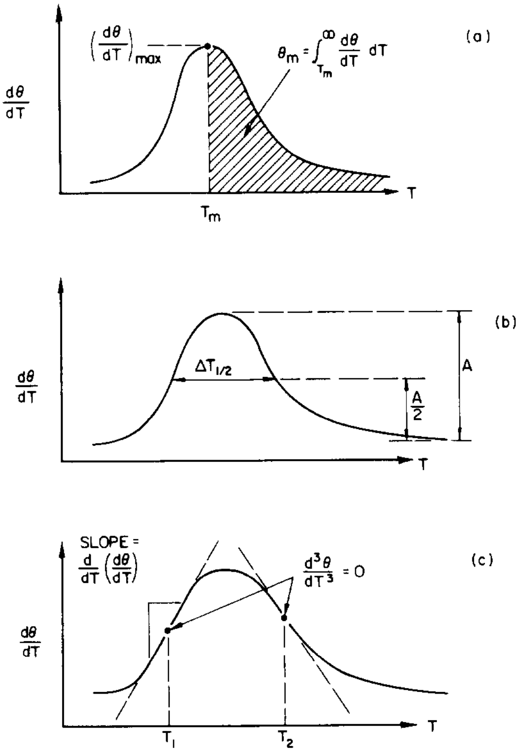

FIG. 1. Information easily available from TPD peak (a) $(d\theta/dt)_{max}$ and θ_m; (b) $\Delta T_{1/2}$ (peak width at half-maximum); (c) inflection points (steepest slopes, $d^3\theta/dT^3 = 0$).

deciding between Cases B and D may be difficult.

The variation of T_m with θ_m (or θ_0) has often been used to distinguish between first- and second-order kinetics in flash desorption studies of nonporous surfaces in vacuum systems (Cases A and C). Inclusion of readsorption as a possibility clouds this historical test. For example, using 20 kcal for the energy term in Eqs. (5)–(8), the calculated shifts in peak temperature T_m as θ_0 varies from 0.1 to 0.9 are given below:

First order, no readsorption	$\Delta T_m = 0°C$
First order, equilibrated readsorption	$\Delta T_m = -11°C$
Second order, no readsorption	$\Delta T_m = -44°C$
Second order, equilibrated readsorption	$\Delta T_m = -85°C$

Thus, neither the existence of $\Delta T_m \neq 0$ nor the sign of ΔT_m provides unambiguous information regarding desorption order or readsorption.

Other approaches to TPD spectra analysis have included width-at-half (and three-quarter) maximum (*3*, *5*) (Fig. 1b) and total peak profile calculations (*1*, *2*, *9*). The former has been considered for Cases A and C (*3*); Cases B and D are examined elsewhere (*2*, *10*). The total peak profile necessarily requires a time-consuming comparison of an entire peak shape.

We now consider an alternative parameter which, for well-defined peaks, is simply determined from Fig. 1c. In the following section, we derive expressions for this parameter and show that determination of its value from a single experiment should distinguish between all four cases under consideration.

TPD ANALYSIS: SHAPE INDEX S

The shape index S was defined by Kissinger (*6*) as the ratio of maximum slope magnitudes (each slope in turn obtained from the two inflection points of a peak); he used this concept to analyze reaction orders in (solid) → (solid + gas) reactions as followed by differential thermal analysis (DTA). Konvalinka and Scholten (*7*) considered the applicability of Kissinger's parameter S to porous catalytic solids characterized by TPD. Carrizosa *et al.* (*8*) subsequently indicated that the DTA equation of Kissinger could not be used in TPD analysis; these authors derived an expression for S for the case of first order desorption with equilibrated readsorption. Below we present a complete analysis of S for all four of the above cases of interest.

The shape index definition appropriate to TPD spectra (*7*) is given by Eq. (9):

$$S \equiv \frac{-(d^2\theta/dT^2)_{T_1}}{(d^2\theta/dT^2)_{T_2}}. \qquad (9)$$

For desorption of order $n = 1$ or 2 with no readsorption,

$$-\frac{d\theta}{dT} = \frac{A}{\beta}\,\theta^{n} e^{-E/RT}. \tag{10}$$

Differentiation and elimination of θ^n using Eq. (10) provides the value of the slope of the TPD peak:

$$\frac{d}{dT}\left(\frac{d\theta}{dt}\right) = \frac{d^2\theta}{dT^2} = \frac{d\theta}{dT}\left(\frac{n}{\theta}\frac{d\theta}{dT} + \frac{E}{RT^2}\right). \tag{11}$$

The inflection points are identified by the roots of $d^3\theta/dT^3 = 0$. Using Eqs. (10) and (11) gives

$$\frac{d^3\theta}{dT^3} = \left(2 - \frac{1}{n}\right)\left(\frac{n}{\theta}\frac{d\theta}{dT}\right)^2 + \frac{3E}{RT^2}\left(\frac{n}{\theta}\frac{d\theta}{dT}\right) + \left(\frac{E}{RT^2}\right)^2 = 0 \tag{12}$$

where RT/E is neglected compared with unity.

The integral of an equation of the form of (10) is reasonably approximated (*4*, *6*, *8*) by Eq. (13) for $n \neq 1$:

$$\frac{1}{(n-1)}\left(\frac{1}{\theta^{n-1}} - \frac{1}{\theta_0{}^{n-1}}\right) = \frac{AR}{\beta E}\,T^2 e^{-E/RT}. \tag{13}$$

Substitution for θ^n from (13) in Eq. (11), and inserting the resulting expression for $d\theta/dT$ into Eq. (12) gives Eq. (14):

$$\left(2 - \frac{1}{n}\right)\left[\frac{n}{n-1}\left(\left(\frac{\theta}{\theta_0}\right)^{n-1} - 1\right)\right]^2 + 3\left(\frac{n}{n-1}\right)\left[\left(\frac{\theta}{\theta_0}\right)^{n-1} - 1\right] + 1 = 0. \tag{14}$$

The coverages at the two inflection points are evaluated from the roots of (14):

$$\frac{\theta}{\theta_0} = \left\{1 + \frac{-3 \pm \left[9 - 4\left(2 - \frac{1}{n}\right)\right]^{1/2}}{2[n/(n-1)](2 - 1/n)}\right\}^{1/(n-1)} \tag{15}$$

For $n = 2$, the roots are $\theta/\theta_0 = (0.789, 0.211)$.

For $n = 1.0$, the corresponding quadratic is

$$\left[\ln\left(\frac{\theta}{\theta_0}\right)\right]^2 + 3\ln\left(\frac{\theta}{\theta_0}\right) + 1 = 0 \tag{16}$$

with solutions

$$\frac{\theta}{\theta_0} = e^{-1.5 \pm 1.25^{1/2}} = (0.68, 0.073).$$

The shape index S is given by the appropriate form of Eq. (17):

$$S \equiv \frac{-(d^2\theta/dT^2)_{T_1}}{(d^2\theta/dT^2)_{T_2}} = \frac{-\left[\frac{d\theta}{dT}\left(\frac{n}{\theta}\frac{d\theta}{dT} + \frac{E}{RT^2}\right)\right]_{T_1}}{\left[\frac{d\theta}{dT}\left(\frac{n}{\theta}\frac{d\theta}{dT} + \frac{E}{RT^2}\right)\right]_{T_2}}. \tag{17}$$

For $n = 1$, Eqs. (16) and (17) yield

$$S = \frac{-\theta_1 \ln\left(\frac{\theta_1}{\theta_0}\right)\left[\ln\left(\frac{u_1}{\theta_0}\right) + 1.0\right]}{\theta_2 \ln\left(\frac{\theta_2}{\theta_0}\right)\left[\ln\left(\frac{\theta_2}{\theta_0}\right) + 1.0\right]}\left(\frac{T_2}{T_1}\right)^4. \tag{18}$$

For $n = 2$, Eqs. (14) and (17) give

$$S = \frac{-\theta_1\left(\frac{\theta_1}{\theta_0} - 1\right)\left[2\left(\frac{\theta_1}{\theta_0}\right) - 1\right]}{\theta_2\left(\frac{\theta_2}{\theta_0} - 1\right)\left[2\left(\frac{\theta_2}{\theta_0}\right) - 1\right]}\left(\frac{T_2}{T_1}\right)^4. \tag{19}$$

For computational convenience, Kissinger used the empirical approximation of $T_2/T_1 \sim 1.08$ for *DTA* spectra (*5*). A survey by us of well-defined *TPD* peaks indicates that $T_2/T_1 \sim 1.1$, ranging from 1.07 to 1.13. The calculated coverages (at the inflection points) and peak shape index (S) values for T_2/T_1 set equal to 1.1 are summarized in Table 1 for various initial coverages, θ_0, and desorption orders of $n = 1,2$. The calculated index S is invariant with respect to initial coverage but is strikingly different for first- or second-order desorptions.

When equilibrium readsorption occurs, Eq. (10) must be replaced by the following equation (20):

TABLE 1

Calculated Shape Index: No Adsorption

θ_0	$n =$	1.0	2.0
1.0	$\theta_1 =$	0.68	0.79
	$\theta_2 =$	0.073	0.21
	$S =$	0.76	1.46
0.75	$\theta_1 =$	0.51	0.59
	$\theta_2 =$	0.055	0.16
	$S =$	0.76	1.46
0.50	$\theta_1 =$	0.34	0.39
	$\theta_2 =$	0.037	0.11
	$S =$	0.76	1.46
0.25	$\theta_1 =$	0.17	0.20
	$\theta_2 =$	0.018	0.053
	$S =$	0.76	1.46

$$\frac{d\theta}{dT} = -\frac{Z}{\beta}\left(\frac{\theta}{1-\theta}\right)^n e^{-E'/RT} \tag{20}$$

where $Z = FA/V_c\nu_m$. It is convenient to define an integral, I_n, arising naturally from Eq. (20) for any reaction order, n:

$$I_n(\theta) \equiv \int_{\theta_0}^{\theta} \left(\frac{1}{\theta} - 1\right)^n d\theta.$$

Then the result of Carrizosa *et al.* (*8*) (after correcting a sign error in their Eq. (9), and recalling that $RT/E' \ll 1$) and Eq. (21) is equivalent to

$$S = \frac{-\left(\frac{\theta_1}{1-\theta_1}\right)^n \left(I_n(\theta_1)\,\frac{n\,I_n(\theta_1)\theta_1^{\,n-1}}{(1-\theta_1)^{n+1}} + 1\right)}{\left(\frac{\theta_2}{1-\theta_2}\right)^n \left(I_n(\theta_2)\,\frac{n\,I_n(\theta_2)\theta_2^{\,n-1}}{(1-\theta_2)^{n+1}} + 1\right)} \left[\frac{T_2}{T_1}\right]^4 \tag{21}$$

where, for $n = 1$

$$I_1(\theta) = \ln\frac{\theta}{\theta_0} - (\theta - \theta_0). \tag{22}$$

For $n = 2$, Eq. (21) is again recovered, with a different function for I_n:

$$I_2(\theta) = \left(\frac{1}{\theta_0} - \frac{1}{\theta}\right) - 2\ln\left(\frac{\theta}{\theta_0}\right) + (\theta - \theta_0). \tag{23}$$

The corresponding calculated coverages at the inflection points and resulting shape indices are given in Table 2. For either desorption order, the shape index S now varies with initial coverage θ_0; the index values differ considerably for $n = 1$ or 2 when $\theta_0 \geq 0.75$.

The calculated shape indices for all four cases of interest are plotted versus initial coverage in Fig. 2. This figure indicates the central result of this paper. *For θ_0 near unity, all four cases appear to be distinguishable.* As TPD measurements are frequently preceded by adsorption at low T_0, achievement of conditions giving $0.75 < \theta_0 \leq 1.0$ is expected to be routine. This figure predicts that calculation of S from slope measurements on a single peak from a single experiment should indicate whether the desorption is first or second order and whether readsorption is absent or equilibrated.

With the reaction order n and the pres-

TABLE 2

Calculated Shape Index: Equilibrated Readsorption

θ_0	$n =$	1.0	2.0
1.0	$\theta_1 =$	0.68	0.69
	$\theta_2 =$	0.073	0.11
	$S =$	0.55	1.32
0.75	$\theta_1 =$	0.56	0.66
	$\theta_2 =$	0.41	0.11
	$S =$	0.69	0.84
0.50	$\theta_1 =$	0.36	0.42
	$\theta_2 =$	0.032	0.09
	$S =$	0.78	0.71
0.25	$\theta_1 =$	0.17	0.20
	$\theta_2 =$	0.018	0.054
	$S =$	0.79	0.73

ence or absence of equilibrated readsorption known, the energy and preexponential terms are calculated from the measured value of $(d\theta/dT)_{\max}$ using the appropriate equations. For no readsorption, for example, we use Eq. (11), which equals zero at T_m, thus

$$E = -\frac{nRT_m^2}{\theta}\left(\frac{d\theta}{dT}\right)_{T_m} \qquad (24)$$

and, from Eq. (10),

$$A = -\frac{\beta(d\theta/dT)_{T_m}}{\theta^n e^{-E/RT_m}}. \qquad (25)$$

In the presence of equilibrated readsorption, the analogs to Eqs. (24) and (25) are Eqs. (24′) and (25′):

$$E' = \frac{-nRT_M^2}{\theta(1-\theta)}\left[\frac{d\theta}{dT}\right]_{T_m} \qquad (24')$$

and

$$A' = \frac{-\beta[d\theta/dT]_{T_m}}{Z'\left(\frac{\theta}{1-\theta}\right)^n e^{-E'/RT_m}} \qquad (25')$$

respectively, where $Z' = F/(V_C\nu_m)$.

All of the desired information, viz. n, E, A, is thus available from relatively simple measurements on a single peak. We have not yet carried out calculations for the more cumbersome case of nonequilibrated readsorption using Eq. (4). The smoothly varying nature of Eq. (4) indicates that the results will be intermediate between no readsorption and equilibrated readsorption. If direct calculation verifies this presumption, then Fig. 2 indicates that for θ_0 near 1.0, we can use the evident guidelines below to determine desorption order without knowing the influence of readsorption (these bounds include allowance for a 10% error in measurement of S):

if $S(\text{expt}) \geq 1.2$, then $n = 2$ (26a)

if $S(\text{expt}) \leq 0.9$, then $n = 1$. (26b)

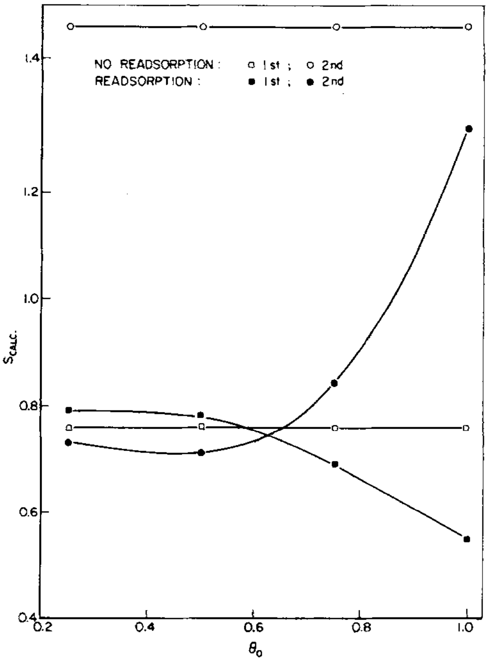

FIG. 2. Predicted shape index S versus initial coverage θ_0 (first- and second-order desorption, presence or absence of equilibrated readsorption).

COMPARISION WITH EXPERIMENT: SHAPE INDEX EVALUATIONS

The S values predicted by the above developments are compared in Table 3 with S values which we determined from well-defined TPD peaks reported in the literature. The initial coverages were apparently unity in all cases. Our determinations of S(expt) are expected to have a possible error of 10–15%, which is not serious enough to bring about confusion regarding desorption order. Examination of Table 3 shows that all 11 results fall within the guidelines suggested by Eqs. (26a,b). Most of the results considered in Table 3 are desorption peaks obtained in vacuum systems, where readsorption is frequently negligible. The three cases involving porous supports suggest that the analyses for no readsorption (C_2H_4 on Al_2O_3) (*14*), equilibrated readsorption (CH_3OH on Al_2O_3) (*19*), and intermediate cases (N_2/N_2H_4 on Ir/Al_2O_3) (*18*) may be appropriate. These experimental results are encouraging, but much further comparison with porous systems is needed before guidelines such as Eqs. (26a,b) are seriously tested.

TABLE 3

Comparison of Theoretical S with Experiment

Experiment	Order[a]	T_m(K)	Reference	S_{expt}	S_{calc}[b]	Percentage difference
CO on Ni	1(N)	440	*3*	0.75	0.76	−1.3
CO on Pt(110)	1(N)	430	*11*	0.87	0.76	+14
CO on ox Pt(110)	1(N)	580	*12*	0.70	0.76	−7.9
C_2H_4 on Pt	1(N)	390	*13*	0.81	0.76	+6.6
C_2H_4 on Al_2O_3	1(N)	500	*14*	0.76	0.76	+0
H_2 on Ni(111)(2 × 1)C	2(N)	290	*15*	1.58	1.46	8.2
H_2 on Cu/Ni	2(N)	350	*16*	1.39	1.46	−4.8
N_2 on W	2(N)		*4*	1.41	1.46	−3.4
$N_2(\beta)$ on W	2(N)	1250	*17*	1.31	1.46	−10
N_2/N_2H_4 on Ir/Al_2O_3	1[c]	540	*18*	0.68	0.76	−10
CH_3OH on Al_2O_3	2(R)	580	*19*	1.29	1.32	−2.3

[a] N, No readsorption; R, with readsorption.

[b] $T_2/T_1 = 1.1$.

[c] Apparently intermediate degree of readsorption.

SOURCES OF EXPERIMENTAL ERRORS

Independent of errors in measuring peak parameters from an actual spectrum, instrumental error and other experimental phenomena may introduce unwanted disguises in the results. Here we discuss several such problems.

Time Lag

An undesired time delay may occur due to, e.g., physical lag in the sensing thermocouple (*20*), or to the physical separation between catalyst and detector. These lags will introduce recorded temperatures which are lower or higher, respectively, than the true temperature. Kinetic parameter determinations based on T_m measurements may be seriously affected (*20*). The shape index is independent of this error if the approximation $(T_2/T_1) = 1.1$ is always used. If the actual inflection point temperatures are used, a 20°C error for a peak with T_1 (true) = 400°K and T_2 (true) = 1.1 × 400 = 440°K gives

$$\left(\frac{T_2}{T_1}\right)^4_{\text{true}} = (1.1)^4 = 1.464$$

and

$$\left(\frac{T_2 + 20}{T_1 + 20}\right)^4_{\text{apparent}} = \left(\frac{460}{420}\right)^2$$
$$= (1.095)^4 = 1.439$$

giving an error of only (100 × 0.025)/1.464 = 1.7% in determining S. Thus, reaction order determination by shape index analysis is affected negligibly by these experimental ΔT errors.

Axial Dispersion

Peak broadening during flow between catalyst and detector will introduce errors in the measured shape index. TPD by its nature involves slow heating rates, of the order of 20°C/min. The peak described above with T_1 = 400°K and T_2 = 440°K will thus be 2 min in length, flowing past the detector. With a linear velocity of 10 cm/sec, the corresponding peak half-width is 10 (cm/sec) × 120 sec = 12 m. In 2 min, the gas molecule axial dispersion distance is (*22*)

$$x_{\text{rms}} \simeq E_0 t^{1/2}$$
$$= [(1.97\ \text{cm/sec})(120\ \text{sec})]^{1/2} \simeq 15.4\ \text{cm}$$

(*22*) which is only 1.2% of the distance between inflection points. Thus, peak broadening should be negligible in altering S.

INTERNAL DIFFUSION DISGUISES

The transient nature of TPD indicated by Eq. (2) indicates that a maximum will always exist in the desorption rate. The balance implied by this equation assumes that C is uniform throughout the desorption volume, i.e., that no serious intrapellet gradients exist. A simple approximation is now developed to guide validation of this assumption.

For a catalytic reaction at steady state, there are no appreciable diffusion gradients within the pellet if (*24*)

$$\frac{\left(\frac{\text{observed reaction rate}}{\text{catalyst volume}}\right) R^2_{\text{pellet}}}{\mathscr{D}_{\text{eff}} \cdot C_0} < 0.3$$

where R_{pellet} is a characteristic pellet dimension, $\mathscr{D}_{\text{eff}}$ is the effective diffusion coefficient (including corrections for tortuosity of pores and porosity of the soid) and C_0 is the external bulk concentration of reactant (i.e., its maximum value in the system).

A corresponding estimate for TPD may be written as the inequality (27):

$$\frac{\left(\nu_m V_c \frac{\partial\theta}{\partial t}\right) R^2}{\mathscr{D}_{\text{eff}} \cdot C_{\max}} < 1. \tag{27}$$

Since $C_{\max}$ will now occur inside the pellet, but we can measure only $C_{\text{bulk}} \equiv C_{\max}/\alpha$, inequality (27) can be written in terms of the measurable external quantity C_{bulk}. At the maximum rate of desorption,

$$\left(\frac{\partial\theta}{\partial t}\right)_{\max} \equiv \beta \left(\frac{d\theta}{dT}\right)_{\max}$$

and the desired inequality is given by the following expression:

$$\frac{\nu_m \beta \left(\frac{d\theta}{dT}\right)_{\max} R^2}{\mathscr{D}_{\text{eff}} \cdot \alpha C_{\text{bulk}}} < 1. \tag{28}$$

Accordingly, those variables available to the experimentalist, namely, heating rate (β) and particle size (R), should satisfy the relation

$$\beta R^2 < \frac{\mathscr{D}_{\text{eff}} \cdot \alpha C_{\text{bulk}}}{\nu_m \left(\frac{d\theta}{dT}\right)_{\max}} \tag{29a}$$

in order that the experiment be free of diffusional influences. Note that as α is ≥ 1, setting $\alpha = 1.0$ in (29) provides a slightly conservative estimate (when (29) is satisfied, α will indeed be near unity).

A numerical example illustrates the importance of this criterion. Suppose a given experiment is characterized by $C_{\text{bulk}} = 0.001$ atm $\sim 5 \cdot 10^{-5}$ moles/liter $= 5 \cdot 10^{-8}$ moles/ml, $\nu_m = 10^{-5}$ moles of sites/cm^3, $\alpha = 1.0$, $\mathscr{D}_{\text{eff}} = 10^{-2}$ cm^2/sec, $(d\theta/dT)_{\max} = 0.0125$ (°K)$^{-1}$. Then an experiment free of diffusional influences requires

$$\beta R^2 < \frac{10^{-2}(\text{cm}^2/\text{sec}) \times 1.0 \times (5 \cdot 10^{-8}\ \text{moles/cm}^3)}{10^{-5}(\text{moles/cm}^3)(1.25 \cdot 10^{-2}\ (°\text{K})^{-1})}$$
$$< 4 \cdot 10^{-3}\ (°\text{K/sec})\text{cm}^2.$$

Even if the pellet radius $R = 0.1$ cm, we need $\beta < 4 \cdot 10^{-3}/(10^{-1})^2 = 4 \cdot 10^{-1}$ °K/sec $= 24$°K/min, which is still achievable with a reasonable heating rate of e.g., 10°K/min.

When readsorption is appreciable, the above criterion needs to include the influence of this phenomenon, which may be appreciable, on catalyst particle relaxation. For a linear isotherm, for example, with binding constant K and an equilibrated readsorption, the effective diffusion coefficient $\mathscr{D}_{\text{eff}}$ is reduced by the factor $(1 + K)$

(*21*), which could reduce $\mathscr{D}_{\text{eff}}$ to very low values. However, the essence of the conditions pertinent to a TPD peak is that, by its observation, we have reached a sufficiently high temperature that the residence time of a molecule on the site is the order of a few minutes. Thus, while K may be appreciable, it will not generally be many orders of magnitude at the desorption temperature of concern.

At the maximum desorption rate, the material is approximately half desorbed. We have the adsorbed phase concentration $= 0.5 \cdot 10^{-5}$ moles/cm^3 and gas phase concentration of $5 \cdot 10^{-8}$ moles/cm^3 giving a dimensionless adsorption equilibrium constant of $K = (5 \cdot 10^{-6})/(5 \cdot 10^{-8}) = 100$. The corresponding effective diffusion coefficient is $\mathscr{D}_{\text{e}} = \mathscr{D}_{\text{eff}}/(1 + K) \sim 10^{-4}$ cm^2/sec. Since very slow heating rates are impractical, maintaining β at 10°C/min ($= 1.6 \cdot 10^{-1}$ °K/sec) would require grinding the catalyst of interest to a size R satisfying inequality (29b):

$$R < \left\{ \left(\frac{\mathscr{D}_{\text{eff}}}{1 + K}\right) \left(\frac{\alpha \cdot C_{\text{bulk}}}{\beta \cdot \nu_{\text{m}} \left(\frac{d\theta}{dT}\right)_{\text{max}}} \right) \right\}^{1/2}$$
$$< \left[\frac{(4 \cdot 10^{-5}\ ^\circ\text{K/sec})\text{cm}^2}{1.6 \cdot 10^{-1} (^\circ\text{K/sec})} \right]^{1/2}$$
$$= 0.16 \text{ mm}. \qquad (29\text{b})$$

The exact criterion needed to ensure a lack of diffusion influence is more subtle. Since C_{bulk} (Eq. (4)), K ($= e^{-G^\circ/RT}$) and $d\theta/dT$ (Eq. (10) or (20)) are all functions of temperature T, R must satisfy the inequality (29a,b) *everywhere* within the range of T which determines the peak shape, e.g., $(T_{\text{m}} - \Delta T) \leq T \leq (T_{\text{m}} + \Delta T)$ (see Figs. 1a and b).

CONCLUSIONS

Shape index (S) analysis of temperature-programmed desorption peaks has here been shown to allow, in theory, discrimination between four important cases involving first- or second-order desorption, with no readsorption or with equilibrated readsorption, when the initial coverage is near unity. Provided that intermediate cases involving nonequilibrated readsorption yield S values intermediate between those for the asymptotic conditions of no and equilibrated readsorption, the guidelines (26a,b) provide a simple indication of desorption reaction order for any degree of readsorption.

The experimental determination of the shape index is not influenced by characteristic errors in temperature measurement or by axial dispersion under typical flow conditions. Some attention should be paid to ensuring lack of diffusional intrusions in the measurements: a simple criterion illustrated by inequalities (29a,b) is proposed and its use examined under a reasonable set of conditions.

We hope that the simplicity of the shape index determination from a single experiment and the information shown here to be directly available from its value will lead to an increased use of this parameter by researchers in catalysis.

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$$E_a \simeq 10^{-1}(\mathrm{cm}^2/\mathrm{sec}) + \frac{1}{48}\,\frac{(0.3\ \mathrm{cm})^2(10\ \mathrm{cm/sec})^2}{10^{-1}\ (\mathrm{cm/sec})}$$

$$= 10^{-1} + \frac{9\cdot 10^{-2}\cdot 10^{2}}{48\cdot 10^{-1}} = 1.97\ \mathrm{cm}^2/\mathrm{sec}.$$

This shifts the estimate to $x_{\mathrm{rms}} = (0.93 \times 120)^{1/2} \gtrsim 10.6$ cm, still only $10.6/1200 \sim 1\%$ of the peak width between inflection points.

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