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LETTERS TO THE EDITORS

Remarks on "Temperature-Programmed Desorption from Porous Catalysts: Shape Index Analysis"

In a recent paper, Ibok and Ollis (*1*) have calculated the "shape index," S, of temperature-programmed desorption curves (TPD curves) as the absolute value of the ratio of the slopes of the tangents of the TPD curve at the inflection points, following its definition in the literature (*2*),

$$S = \left|\frac{(d^2\theta/dt^2)_1}{(d^2\theta/dt^2)_2}\right| . \qquad (1)$$

According to these authors, for initial coverages close to one, a single measurement of S on an experimental TPD curve could easily discriminate among four important cases: (i) first-order desorption without readsorption; (ii) first-order desorption with equilibrated readsorption; (iii) second-order desorption without readsorption; and (iv) second-order desorption with equilibrated readsorption.

The scope of this Letter is, first of all, to remark that Ibok and Ollis's reported S values for second-order desorption with equilibrated readsorption are probably miscalculated. This fact is important since it introduces some doubts on the general conclusions reached in their paper. Furthermore, we will also stress that the value of the "shape index" corresponding to given desorption kinetics strongly depends on E/RT (*3*), and, therefore, it is necessary to revise the conclusions reached in their paper based on the assumption that $E \gg RT$ (i.e., $RT/E \approx 0$).

Desorption of gases adsorbed on a solid surface fits the general law:

$$-\frac{d\theta}{dt} = \frac{A}{\beta} \cdot \exp(-E/RT) \cdot f(\theta), \qquad (2)$$

where θ represents the surface coverage; β the heating rate; A the preexponential factor of Arrhenius if the desorption takes place without readsorption and it stands for $\exp(\Delta S/RT)$ (ΔS being the adsorption entropy) when there is equilibrated readsorption of the desorbed gases; E the heat of adsorption or the activation energy of desorption, depending on whether the desorption process occurs with or without equilibrated readsorption, respectively; and $f(\theta)$ a function that depends on the reaction kinetics. Algebraic expressions for $f(\theta)$ are given in Table 1 for the four kinetics mentioned above, together with their first and second derivatives, $f'(\theta)$ and $f''(\theta)$, required in further calculations below.

Equation (2) can be integrated between the initial coverage, θ_0, and θ by taking into account the expression for the integral of the Arrhenius law (*4*) to yield:

$$g(\theta) = -\int \frac{d\theta}{f(\theta)} = \frac{ART^2}{\beta \cdot E} \cdot h(\epsilon) \cdot \exp(-E/RT), \qquad (3)$$

where $h(\epsilon)$ is a function given by the expression

$$h(\epsilon) = 1 - \frac{2!}{\epsilon} + \frac{3!}{\epsilon^2} - \cdots \pm \frac{(-1)^n(n+1)!}{\epsilon^n} \qquad (4)$$

and $\epsilon = E/RT$. Expressions for $g(\theta)$ for all four kinetics have been also included in Table 1.

By using the calculation method previously described in the literature (*3*) and used by Ibok and Ollis in their paper (*1*), the following general expression can be obtained from Eqs. (2) and (3):

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TABLE 1

Algebraic Expressions of $f(\theta), f'(\theta), f''(\theta)$, and $g(\theta)$ for Different Desorption Kinetics

Kinetics	$f(\theta)$	$f'(\theta)$	$f''(\theta)$	$g(\theta)$
First-order desorption without readsorption	θ	1	0	$-\ln(\theta/\theta_0)$
First-order desorption with equilibrated readsorption	$\frac{\theta}{1-\theta}$	$\frac{1}{(1-\theta)^2}$	$\frac{2}{(1-\theta)^3}$	$\theta - \theta_0 - \ln(\theta/\theta_0)$
Second-order desorption without readsorption	θ^2	2θ	2	$(1/\theta) - (1/\theta_0)$
Second-order desorption with equilibrated readsorption	$\frac{\theta^2}{(1-\theta)^2}$	$\frac{2\theta}{(1-\theta)^3}$	$\frac{2+4\theta}{(1-\theta)^4}$	$\frac{1}{\theta} - \frac{1}{\theta_0} - \theta + \theta_0 + 2\ln(\theta/\theta_0)$

$$S = \left| \frac{f(\theta_1) \cdot g(\theta_1) \cdot [(1/h(\epsilon)) \cdot f'(\theta_1) \cdot g(\theta_1) - 1]}{f(\theta_2) \cdot g(\theta_2) \cdot [(1/h(\epsilon)) \cdot f'(\theta_2) \cdot g(\theta_2) - 1]} \right| \cdot \left(\frac{T_2}{T_1}\right)^4 = S_1 \left(\frac{T_2}{T_1}\right)^4, \tag{5}$$

where θ_1 and θ_2 are the values of θ at the first and second inflection points of the TPD curves, given by the roots of the equation

$$\frac{g(\theta_i)^2}{h(\epsilon)^2} f''(\theta_i) \cdot f(\theta_i) + f'(\theta_i)^2 - \frac{3}{h(\epsilon)} \cdot f'(\theta_i) \cdot g(\theta_i) + \left(1 - \frac{2RT}{E}\right) = 0. \tag{6}$$

If we assume, following again Ibok and Ollis's paper *(1)* that $RT/E \simeq 0$ (i.e., $h(\epsilon) = 1$), expressions of S can be deduced for all four kinetics by substituting into Eq. (5) the expressions summarized in Table 1:

(i) *Without readsorption*
First order

$$S = \left| \frac{\theta_1 \cdot \ln(\theta_1/\theta_0) \cdot [\ln(\theta_1/\theta_0) + 1]}{\theta_2 \cdot \ln(\theta_2/\theta_0) \cdot [\ln(\theta_2/\theta_0) + 1]} \right| \cdot \left(\frac{T_2}{T_1}\right)^4. \tag{7}$$

Second order

$$S = \left| \frac{\theta_1(\theta_1/\theta_0 - 1)[2(\theta_1/\theta_0) - 1]}{\theta_2(\theta_2/\theta_0 - 1)[2(\theta_2/\theta_0) - 1]} \right| \cdot \left(\frac{T_2}{T_1}\right)^4. \tag{8}$$

(ii) *With equilibrated readsorption*
First order

$$S = \left| \frac{(\theta_1/(1-\theta_1)) \cdot g(\theta_1) \cdot [(1/(1-\theta_1)^2) \cdot g(\theta_1) - 1]}{(\theta_2/(1-\theta_2)) \cdot g(\theta_2) \cdot [(1/(1-\theta_2)^2) \cdot g(\theta_2) - 1]} \right| \cdot \left(\frac{T_2}{T_1}\right)^4. \tag{9}$$

Second order

$$S = \left| \frac{(\theta_1/(1-\theta_1)) \cdot g(\theta_1) \cdot [(2\theta_1/(1-\theta_1)^3) \cdot g(\theta_1) - 1]}{(\theta_2/(1-\theta_2)) \cdot g(\theta_2) \cdot [(2\theta_2/(1-\theta_2)^3) \cdot g(\theta_2) - 1]} \right| \cdot \left(\frac{T_2}{T_1}\right)^4. \tag{10}$$

It is easily shown that Eqs. (9) and (10) can be generalized in the form,

$$S = \left| \frac{(\theta_1/(1-\theta_1))^n \cdot g(\theta_1) \cdot [(n \cdot g(\theta_1) \cdot \theta_1^{n-1})/(1-\theta_1)^{n+1} - 1]}{(\theta_2/(1-\theta_2))^n \cdot g(\theta_2) \cdot [(n \cdot g(\theta_2) \cdot \theta_2^{n-1})/(1-\theta_2)^{n+1} - 1]} \right| \cdot \left(\frac{T_2}{T_1}\right)^4 \tag{11a}$$

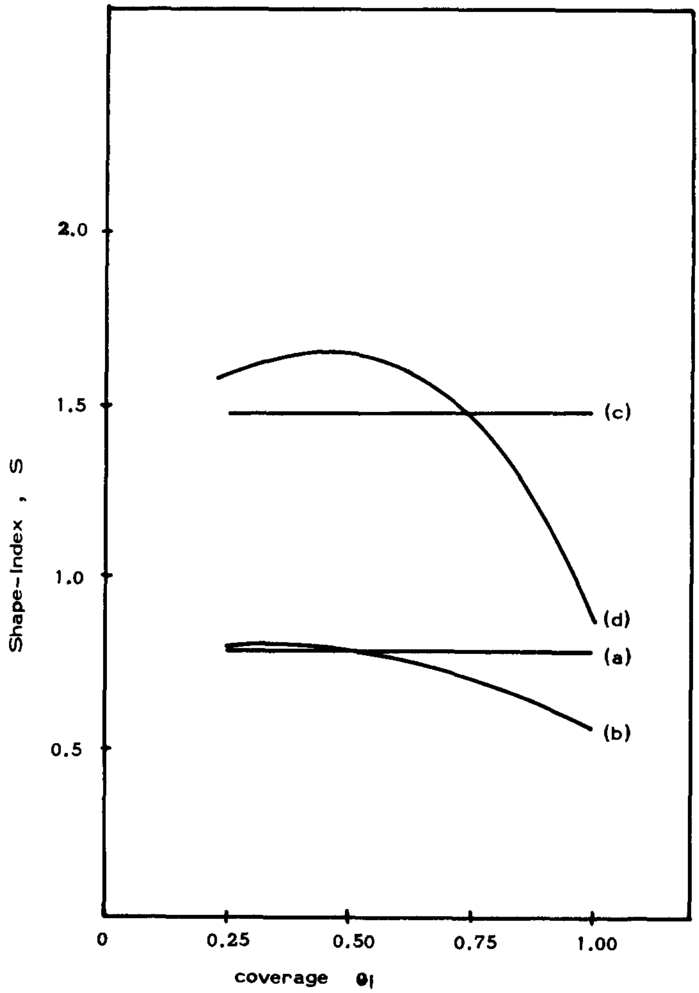

FIG. 1. "Shape index" vs coverage ($E/RT = \infty$, $T_2/T_1 = 1.1$) for: (a) first-order desorption without readsorption, (b) first-order desorption with equilibrated readsorption, (c) second-order desorption without readsorption, (d) second-order desorption with equilibrated readsorption.

and, taking into account the relationship between the function $I_n(\theta)$, introduced by Ibok and Ollis (*1*), and our $g(\theta)$ function in Table 1 (i.e., $g(\theta) = -I_n(\theta)$), Eq. (11a) becomes

$$S = \left| \frac{(\theta_1/(1-\theta_1))^n \cdot I_n(\theta_1) \cdot [(n \cdot I_n(\theta_1) \cdot \theta_1^{n-1})/(1-\theta_1)^{n+1} + 1]}{(\theta_2/(1-\theta_2))^n \cdot I_n(\theta_2) \cdot [(n \cdot I_n(\theta_2) \cdot \theta_2^{n-1})/(1-\theta_2)^{n+1} + 1]} \right| \cdot \left(\frac{T_2}{T_1}\right)^4 \cdot \quad (11\text{b})^1$$

Thus, Eqs. (7), (8), and (11b) developed in Ibok and Ollis's paper (*1*) are only particular cases of the most general Eq. (5), which had been previously deduced by us (*3*). In actual fact, "shape indexes" in Tables 1 and 2 of Ibok and Ollis's paper (*1*) for different kinetics show a very good agreement with those calculated from the S_1 values previously reported by us (*3*), except for second-order desorption with equilibrated readsorption. This discrepancy seems to arise from some miscalculations probably introduced during computation af-

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[1] A printing error exists in the equivalent Eq. (21) in Ibok and Ollis's paper.

ter substitution of the proper values of θ_1 and θ_2 into Eq. (11b).

The S values recalculated by us for all four cases using Eq. (5) and taking $T_2/T_1 = 1.1$ have been plotted vs initial coverage in Fig. 1. This figure corresponds to Fig. 2 in Ibok and Ollis's paper (*1*) and shows that the "shape index" for the second-order desorption with equilibrated readsorption almost coincides with that of a first-order desorption without readsorption when $\theta_0 = 1$. Therefore, it would be troublesome to discern between these two kinetics from the measurement of S on an experimental TPD curve, as suggested by Ibok and Ollis (*1*).

However, there is a second point that should be examined before taking for granted the conclusions reached by Ibok and Ollis (*1*). A perusal of the literature indicates that experimental values of E/RT in TPD are, in general, lower than ca. 40 and in this range a strong dependence of S on E/RT should be expected (*3*). Changes in the "shape indexes" previously deduced by us (*3*) for TPD curves with $\theta_0 = 1$ vs E/RT have been plotted in Fig. 2. It can be seen that the "shape index" corresponding to every kinetics case changes within a

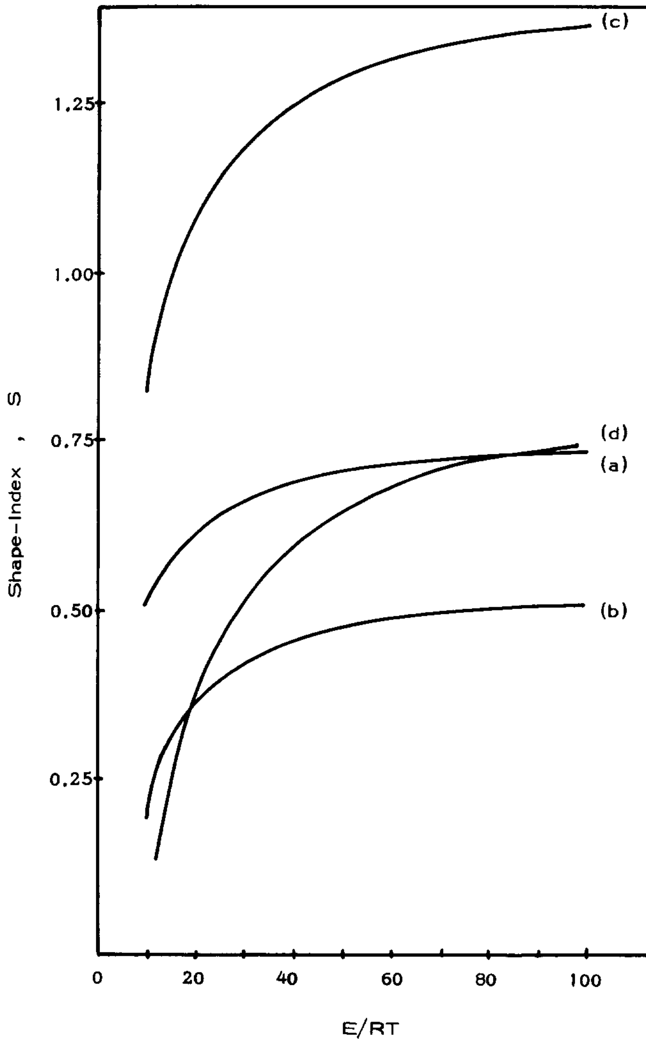

FIG. 2. "Shape index" vs E/RT at $\theta_0 = 1.0$ ($T_2/T_1 = 1.1$). Identification of the curves as in Fig. 1.

broad range of values depending on E/RT, and shows a different dependence in each case. Moreover, changes are particularly important for E/RT within the experimental range. Thus, an unambiguous determination of the actual kinetics of a desorption process from one measurement of S only without any further information (e.g., E/RT or/and θ_0) seems to be rather difficult.

Finally, it is interesting to remark here that some of the problems stated above might be avoided by using a hyperbolic heating schedule (i.e., $d(1/T) = -b\,dt$). In such a case, one of us (*5*) has deduced that the "shape index" of TPD curves obtained in this way must be independent on both E/RT and T_2/T_1, whatever the actual kinetics followed by the desorption process. Therefore, in this case the "shape index" analysis might be used to unambiguously determine the desorption kinetics, though to our knowledge, it has not been applied to date.

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