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STUDY OF THE "SHAPE INDEX" IN THE ANALYSIS OF TEMPERATURE-PROGRAMMED DESORPTION CURVES

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ABSTRACT

Kissinger's "Shape Index" (SI) method, previously applied to determine the kinetic order of thermal decompositions of solids studied by DTA or DTG, has been assessed in connection with its use in TPD-kinetic analysis. Results indicate that the "shape index" of a TPD-peak depends on $\Delta H/RT$ and T_2/T_1 (i.e., the enthalpy of adsorption or the energy of activation for desorption, and the ratio between the inflection point temperatures), while when readsorption of the desorbed species takes place, dependence on the initial coverage, θ_0, is also observed. The method has been applied to determine the kinetic order of a "theoretical" TPD-peak previously built up leading to correct values of that parameter. The possible use of this method in the study of desorption processes by TPD is discussed.

INTRODUCTION

Thermal decomposition reactions of solids following the general law

$$\frac{d\alpha}{dt} = A \cdot e^{-E/RT}(1 - \alpha)^n \qquad (1)$$

have been examined by Kissinger [1], who has formulated a method of study which allows the determination of the values of n by measuring the "shape index", S, of curves obtained by differential thermal analysis (DTA) or derivatographic thermogravimetry (DTG). According to this author, a relationship exists between both parameters in the form

$$n = 1.26\, S^{1/2} \qquad (2)$$

assuming that the ratio T_1/T_2 between the temperatures at the inflection points of the curves remains almost constant close to 1.08. Lately, the method has been successfully [2] extended to the study of solid decompositions fitting kinetics different from those stated by eqn. (1).

In a recent paper, Konvalinka and Scholten [3] have applied Kissinger's critera to TPD-diagrams of hydrogen weakly adsorbed on the surface of palladium to examine the desorption kinetics of this species. The conclusions obtained by this procedure have been criticized by some [4] on the basis of the difference in the kinetic equations developed in the TPD-method with regard to those used for performing the kinetic analysis of the thermal decomposition of solids. In particular, there is no reason, a priori, for assuming that, for instance, both DTA-diagrams of a first-order decomposition of a solid and TPD-curves of a first-order desorption processes with freely occurring readsorption would have the same "shape indexes" as Konvalinka and Scholten [3] have assumed.

The scope of the present work was to explore in more detail the possibilities of "shape indexes" of TPD-curves of first- and second-order desorption processes (with and without freely occurring readsorption) to analyse kinetic order according to Kissinger's "SI-method" in order to determine the actual kinetics of desorption of gases from solid surfaces.

THEORETICAL

Desorption of gases previously adsorbed on solid surfaces fits the general law

$$-\frac{\mathrm{d}\theta}{\mathrm{d}t} = A^* \cdot \mathrm{e}^{-\Delta H/RT} \cdot \mathrm{f}(\theta) \qquad (3)$$

or

$$-\frac{\mathrm{d}\theta}{\mathrm{d}T} = \frac{A^*}{\beta} \cdot \mathrm{e}^{-\Delta H/RT} \cdot \mathrm{f}(\theta) \qquad (4)$$

where θ represents the surface coverage; β is the heating rate; A^* is the pre-exponential factor of Arrhenius if the desorption takes place without readsorption, and stands for $\exp(\Delta S/R)$, ΔS being the adsorption entropy when there is readsorption of the desorbed gases; ΔH is the heat of adsorption or the activation energy (i.e., E_d) of desorption, depending on whether the desorption process occurs with or without readsorption, respectively; $\mathrm{f}(\theta)$ is a function depending on the reaction kinetics. Algebraic expressions for $\mathrm{f}(\theta)$ are given in Table 1 for different desorption kinetics together with their first and second derivatives, $\mathrm{f}'(\theta)$ and $\mathrm{f}''(\theta)$.

According to Kissinger [1], the "shape index" is defined as the absolute value of the ratio of the slopes of the tangents to the TPD-curve at the inflection points, and can be expressed analytically as

$$S = \left| \frac{(\mathrm{d}^2\theta/\mathrm{d}t^2)_1}{(\mathrm{d}^2\theta/\mathrm{d}t^2)_2} \right| = \frac{a}{b} \qquad (5)$$

where subscripts 1 and 2 refer to the values of $\mathrm{d}^2\theta/\mathrm{d}t^2$ at the first and second inflection points, respectively (i.e., where $\mathrm{d}^3\theta/\mathrm{d}t^3 = 0$). The meaning of a and b is illustrated in Fig. 1 for the "theoretical" TPD-curve deduced in a previous paper [5].

Differentiating eqn. (3), substituting our own eqn. (3) and collecting terms, we obtain

$$\frac{\mathrm{d}^2\theta}{\mathrm{d}t^2} = \left[\frac{\mathrm{f}'(\theta)}{\mathrm{f}(\theta)} \cdot \frac{\mathrm{d}\theta}{\mathrm{d}t} + \frac{\beta\Delta H}{RT^2}\right] \frac{\mathrm{d}\theta}{\mathrm{d}t} \qquad (6)$$

Integrating eqn. (3) between the initial coverage, θ_0, and θ, and taking

TABLE 1

Algebraic expressions of $f(\theta)$, $f'(\theta)$, $f''(\theta)$ and $g(\theta)$ for different desorption kinetics

Kinetics	Symbol	$f(\theta)$	$f'(\theta)$	$f''(\theta)$	$g(\theta)$
First-order without readsorption	1W	θ	1	0	$-\ln(\theta/\theta_0)$
First-order with readsorption	1R1	$\frac{\theta}{1-\theta}$	$\frac{1}{(1-\theta)^2}$	$\frac{2}{(1-\theta)^3}$	$\theta-\theta_0-\ln(\theta/\theta_0)$
Second-order without readsorption	2W	θ^2	2θ	2	$\frac{1}{\theta}-\frac{1}{\theta_0}$
Second-order with second-order readsorption	2R2	$\frac{\theta^2}{(1-\theta)^2}$	$\frac{2\theta}{(1-\theta)^3}$	$\frac{2+4\theta}{(1-\theta)^4}$	$\frac{1}{\theta}-\frac{1}{\theta_0}-\theta+\theta_0+2\ln(\theta/\theta_0)$

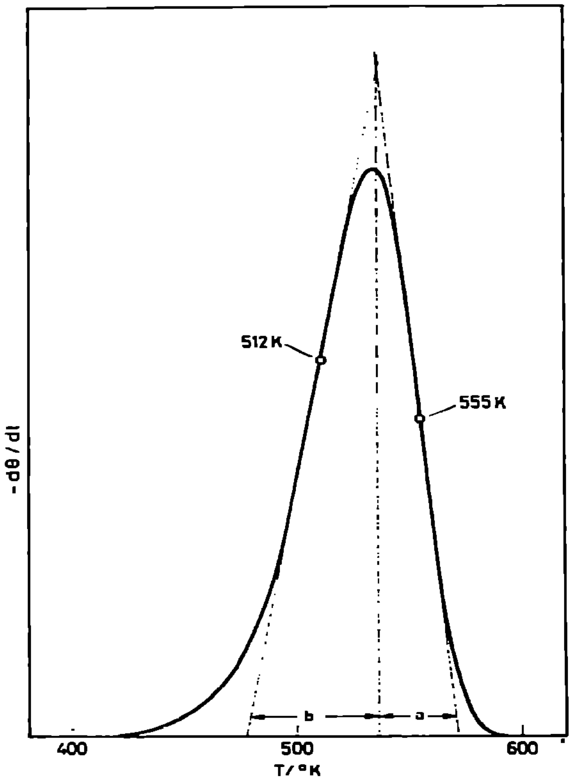

Fig. 1. "Theoretical" TPD-curve from ref. 5, showing the graphical method of calculating the "shape index" S = a/b: a = 35 K; b = 55 K; T_1 = 512 K; T_2 = 555 K; T_M = 535 K.

into account the expression for the integral of the Arrhenius equation [4], we may write

$$g(\theta) = \frac{ART^2}{\beta \Delta H} \cdot h(\epsilon) \cdot e^{-\Delta H/RT} \tag{7}$$

h(ϵ) being a function given by the expression

$$h(\epsilon) = 1 - \frac{2!}{\epsilon} + \frac{3!}{\epsilon^2} - \ldots \pm \frac{(-1)^n(n+1)!}{\epsilon^n} \tag{8}$$

where $\epsilon = \Delta H/RT$. Expressions for g(θ) for the different kinetics have been included in Table 1.

From eqns. (3) and (7) we obtain

$$\frac{d\theta}{dt} = -\frac{\beta \Delta H}{RT^2} \cdot \frac{1}{h(\epsilon)} \cdot f(\theta) \cdot g(\theta) \tag{9}$$

Setting the first derivative of eqn. (6) equal to zero, substituting in eqn. (6) and taking into account the value of dθ/dt given by eqn. (9), we may obtain the condition that must be fulfilled by θ at the inflection points, after rearrangement in the form

$$\frac{g(\theta_i)^2}{h(\epsilon)^2}\left[f''(\theta_i) \cdot f(\theta_i) + f'(\theta_i)^2\right] - \frac{3}{h(\epsilon)} \cdot f'(\theta_i) \cdot g(\theta_i) + \left(1 - \frac{2RT}{\Delta H}\right) = 0 \tag{10}$$

TABLE 2

Algebraic expressions of θ_i coverages for different kinetics

Kinetics[a]	Equation	Remarks
1W	$\theta_i = \theta_0 \exp\left[h(\varepsilon)\left(\frac{-3 \pm a}{2}\right)\right]$	$a = \sqrt{9 - 4\left(1 - \frac{2RT}{\Delta H}\right)}$
1R1	$\frac{1 + 2\theta_i}{(1-\theta_i)^4}(-\ln\theta_i + \theta_i - C_0)^2 \frac{1}{h(\varepsilon)^2} - \frac{3}{(1-\theta_i)^2}(-\ln\theta_i - \theta_i - C_0)\frac{1}{h(\varepsilon)} + \left(1 - \frac{2RT}{\Delta H}\right) = 0$	$C_0 = -\ln\theta_0 + \theta_0$
2W	$\theta_i = \theta_0\left[1 - \frac{h(\varepsilon)(3 \pm b)}{6}\right]$	$b = \sqrt{9 - 6\left(1 - \frac{2RT}{\Delta H}\right)}$
2R2	$\frac{4\theta_i + 6}{(1-\theta_i)^6}\left(\frac{1}{\theta_i} + 2\ln\theta_i - \theta_i - C_0\right)^2 \frac{\theta_i^2}{h(\varepsilon)^2} - \frac{6}{h(\varepsilon)}\frac{\theta_i}{(1-\theta_i)^3}\left(\frac{1}{\theta_i} + 2\ln\theta_i - \theta_i - C_0\right) + \left(1 - \frac{2RT}{\Delta H}\right) = 0$	$C_0 = \frac{1}{\theta_0} + 2\ln\theta_0 - \theta_0$

[a] Symbols as in Table 1.

TABLE 3

Algebraic expressions for S_1 for different desorption kinetics

Kinetics[a]	S_1 function	Remarks
1W	$S_1 = \left\lvert \dfrac{(a-1)(3-a)\exp\left[-h(\epsilon)\dfrac{3-a}{2}\right]}{(a+1)(3+a)\exp\left[-h(\epsilon)\dfrac{3+a}{2}\right]} \right\rvert$	$a = \sqrt{9-4\left(1-\dfrac{2RT}{\Delta H}\right)}$
1R1	$S_1 = \left\lvert \dfrac{\left[\dfrac{1}{h(\epsilon)}\dfrac{-\ln\theta_1+\theta_1-C_0}{(1-\theta_1)^2}-1\right]\dfrac{\theta_1}{1-\theta_1}(-\ln\theta_1+\theta_1-C_0)}{\left[\dfrac{1}{h(\epsilon)}\dfrac{-\ln\theta_2+\theta_2-C_0}{(1-\theta_2)^2}-1\right]\dfrac{\theta_2}{1-\theta_2}(-\ln\theta_2+\theta_2-C_0)} \right\rvert$	$C_0 = -\ln\theta_0+\theta_0$
2W	$S_1 = \left\lvert \dfrac{(3-a)[1-\frac{1}{6}h(\epsilon)(3-a)]}{(3+a)[1-\frac{1}{6}h(\epsilon)(3+a)]} \right\rvert$	$b = \sqrt{9-6\left(1-\dfrac{2RT}{\Delta H}\right)}$
2R2	$S_1 = \left\lvert \dfrac{\left[\dfrac{2\theta_1}{h(\epsilon)}\dfrac{2\ln\theta_1-\theta_1+1/\theta_1-C_0}{(1-\theta_1)^3}-1\right]\dfrac{\theta_1^2}{(1-\theta_1)^2}(2\ln\theta_1-\theta_1+1/\theta_1-C_0)}{\left[\dfrac{2\theta_2}{h(\epsilon)}\dfrac{2\ln\theta_2-\theta_2+1/\theta_2-C_0}{(1-\theta_2)^3}-1\right]\dfrac{\theta_2^2}{(1-\theta_2)^2}(2\ln\theta_2-\theta_2+1/\theta_2-C_0)} \right\rvert$	$C_0 = \dfrac{1}{\theta_0}+2\ln\theta_0-\theta_0$

[a] Symbols as in Table 1.

TABLE 4

Calculated S_1 values for different desorption kinetics

Kinetics[a]	Coverage	$\Delta H/RT$ values							
		10	20	30	40	50	70	100	∞
1W	$0 \leqslant \theta_0 \leqslant 1$	0.345	0.422	0.452	0.468	0.478	0.490	0.499	0.521
1R1	$\theta_0 = 1.00$	0.132	0.247	0.287	0.309	0.321	0.336	0.348	0.375
	$\theta_0 = 0.75$	0.263	0.352	0.388	0.408	0.419	0.433	0.444	0.471
	$\theta_0 = 0.50$	0.328	0.415	0.450	0.468	0.480	0.493	0.504	0.530
	$\theta_0 = 0.25$	0.345	0.428	0.460	0.478	0.488	0.501	0.511	0.535
2W	$0 \leqslant \theta_0 \leqslant 1$	0.562	0.735	0.809	0.851	0.877	0.909	0.935	1.000
2R2	$\theta_0 = 1.00$	0.011	0.245	0.349	0.404	0.437	0.478	0.510	0.589
	$\theta_0 = 0.75$	0.471	0.637	0.718	0.766	0.797	0.835	0.866	0.946
	$\theta_0 = 0.50$	0.585	0.785	0.875	0.928	0.961	1.003	1.036	1.122
	$\theta_0 = 0.25$	0.585	0.776	0.859	0.907	0.937	0.975	1.005	1.081

[a] Symbols as in Table 1.

Equations obtained for each of the desorption kinetics quoted in Table 1 after substituting the corresponding functions $f(\theta)$, $f'(\theta)$, $f''(\theta)$, and $g(\theta)$ in eqn. (10) and collecting terms, are summarized in Table 2. In the case of desorptions without freely occurring readsorption, the solution for θ_i can be easily obtained; however, in the other cases the solutions must be calculated using a computer program.

From eqns. (5), (6), and (9), the "shape index" of the TPD-curve can be expressed in the form

$$S = \left| \frac{f(\theta_1)g(\theta_1)[(1/h(\epsilon)f'(\theta_1)g(\theta_1) - 1]}{f(\theta_2)g(\theta_2)[(1/h(\epsilon)f'(\theta_2)g(\theta_2) - 1]} \right| \cdot \left(\frac{T_2}{T_1}\right)^4 = S_1 \cdot \left(\frac{T_2}{T_1}\right)^4 \qquad (11)$$

where θ_1 and θ_2 refer to the solutions of eqn. (10) at the first and second inflection points, respectively.

Table 3 gives the expressions of S_1 for each of the desorption kinetics included in Table 1. We can see that the expression for "shape index" of a TPD-curve following kinetics 1W and 2W depends only on the values of both $\Delta H/RT$ and T_2/T_1, while in the case of desorptions with freely occurring readsorption, S_1 is also strongly dependent upon the initial coverage, θ_0. This is clearly shown in Table 4, which includes the values of S_1 calculated for the different desorption kinetics, as a function of both $\Delta H/RT$ and θ_0. We can see that at high coverages the values of S_1 are different enough to allow the unambiguous determination of the desorption kinetics. However, if decreasing coverages are used, data in Table 4 indicate that the "shape index" of TPD-curves of the kinetics with freely occurring readsorption would approach values corresponding to those without readsorption. Thus, at low coverages it would be rather difficult to differentiate between processes with and without readsorption although it is always possible to decide between the kinetics of first and second order. The analysis of the variation of S_1 with θ_0 seems, therefore, of interest to indicate whether readsorption is taking place during the TPD-scanning process.

RESULTS AND DISCUSSION

In order to check the application of the methods of kinetic analysis, the TPD-curve shown in Fig. 1 was calculated by the procedure described elsewhere [5], assuming a heating rate of 20°C $\min^{-1}$, an initial coverage $\theta_0 = 1$, and the following kinetic parameters: $E_d = 24$ kcal mole^{-1} and $A = 10^8$ sec^{-1}. A first-order desorption without readsorption was assumed. The value of $S_1 = 0.43$ obtained from Fig. 1 is in very good agreement with the expected one of 0.435 as calculated from the assumed first-order desorption without freely occurring readsorption by interpolating in Table 4, after taking into account $E/RT = 23$.

On the other hand, we have analyzed the shape indexes of TPD-curves of desorption of benzene from the zeolites NaY and NiCaY obtained by Kharlamov et al. [6], and reproduced in Fig. 2. These authors have concluded, by using conventional methods of kinetic analysis, that a first-order desorption without freely occurring readsorption takes place on both samples. The acti-

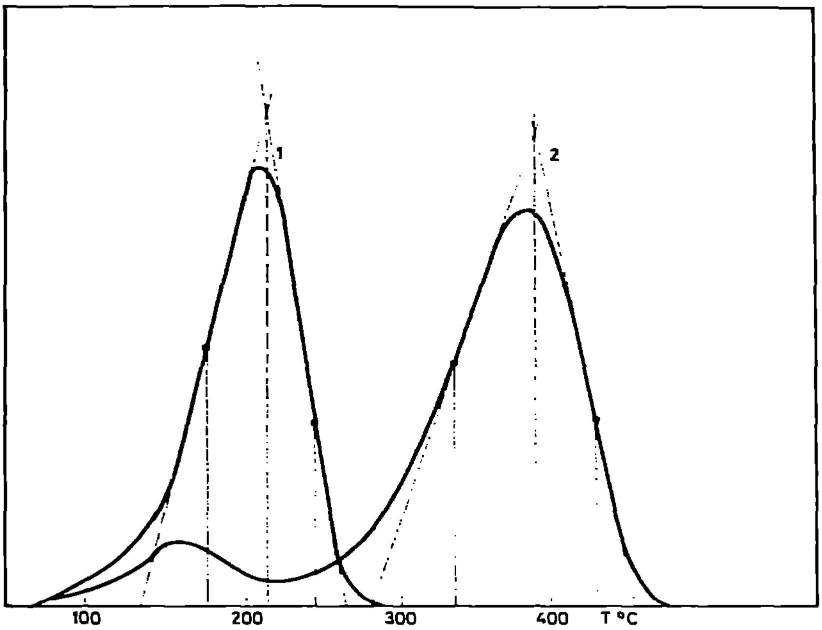

Fig. 2. TPD-curves for desorption of benzene from NaY (1) and NiCaY (2) zeolites, according to Kharlamov et al. [6].

vation energies reported [6] were 12.5 and 21 kcal $mole^{-1}$ on the NaY and NiCaY specimens, respectively.

The values of S_1 calculated from the TPD-curves in Fig. 2 for the desorption of benzene from NaY and NiCaY were 0.34 and 0.36, in very good agreement with those calculated (0.37 and 0.39, respectively) by interpolating the data in Table 4 after taking into account the corresponding values of $\Delta H/RT$.

In summary, we may conclude that the analysis of the "shape index" of single TPD-curves of desorption processes from solid surfaces might represent, if properly used, an easy and quick procedure for determining kinetics of desorption, although a detailed study may be required to examine the influence of the initial coverage on the "shape index" to definitively decide if the reaction takes place with or without readsorption.

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